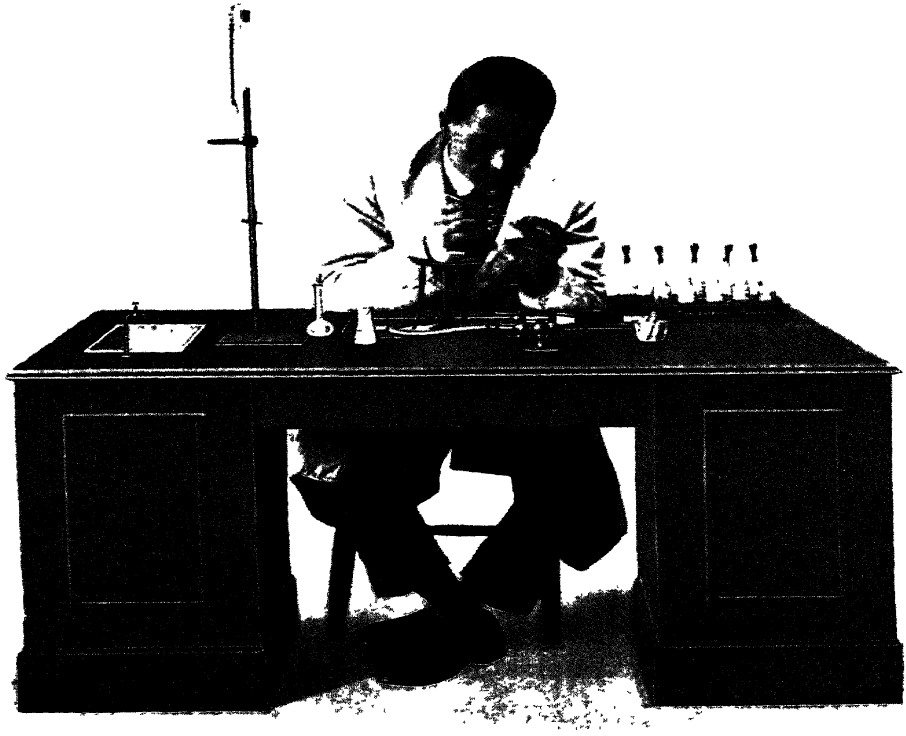
PRACTICAL CHEMISTRY BY MICRO-METHODS

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STUDENT EXAMINING THE EFFECT OF MIXING TWO DROPS

(*See coloured plate facing page* 65)

Practical Chemistry by Micro-Methods

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Preface

It must be evident to many that the time has come for a change in some of the methods of teaching practical chemistry. Classes seem to get larger every year, and the standard is being gradually raised. Much which was done in the first year of a university course must be pushed into the schoolboy's curriculum. It follows that many experiments which could once be performed by each individual must perforce be omitted, and there is a tendency to meet the situation by adapting the practical course rather to the convenience of the laboratory than to the individual needs of the students. The majority who come to the chemical department to-day, are applying themselves to the science as a means and not as an end, and, seeing how divergent these ends are, it is a pity that the training must so often be the same. At the best this but a compromise.

Organic chemistry, particularly, is neglected because of the expense of many of the reagents and the danger of working with large quantities of inflammable materials.

The method of practical micro chemistry is that of working with minute quantities of material, specks of solids, drops of liquids. With this method the difficulties which would hamper many a laboratory will be found to vanish. A student, for example, may without danger prepare a few ccs. of gases, however inflammable or explosive, and he can study the properties of such solvents as alcohol, ether, chloroform or benzene by the use of drops without danger to himself or anxiety to his teacher.

There is nothing which at present is done by students with large apparatus that cannot be done with the micro-method, but there is much that can be done with small apparatus that is sheer waste when done on the larger scale.

With small reagent bottles and small apparatus the benches and general equipment of the laboratory may be greatly simplified. Everything is easier to find and to handle. A student's whole outfit may be put upon a tea-tray, and with his laboratory thus all at hand the student may sit down to his work with consequent

sparing of fatigue to himself and to his teacher. The class-room, whatever the stage of the work, becomes a place of peace and quiet, and the foul atmosphere so often the result of work on a large scale, is avoided. This means a great gain from the point of view of the student's health, a matter which in science teaching is often sadly neglected.

The methods of micro chemistry are exceedingly rapid, for example, by the use of the table on page 65, one of my staff was able to identify the bases of fifteen unknown simple salts in ten minutes with only one doubtful case. This, I think, must be a record.

Such rapid work is the result of using drops, and employing one glass slide instead of several test-tubes. Several reactions may be viewed simultaneously, and by the aid of a pocket lens, studied with a care which is not possible with the test-tube.

One drop of a solution divided into three parts suffices in many cases to characterise at once an unknown base.

After the reaction the slide is washed and dried in a second and ready for the next test.

With this sparing of time it follows that much more work can be got into the working hours, and in consequence studies which were once spread over many years may be condensed into a few. The economy also in energy and in expense is enormous, with the result that it is possible to cover a much broader field of study.

This book is intended for schools or for the earlier part of a university course, and it covers the practical work required by the conjoint boards of the Royal Colleges of Physicians and Surgeons. While describing the methods of micro chemistry, it indicates also how a practical course may be broadened to include exercise, in elementary physical chemistry, qualitative analysis, volumetric analysis, and a brief introduction to organic chemistry is given. sufficient to give the student a taste for this fascinating subjects

I would like, in concluding, to express my thanks to my colleague, Mr. W. M. Colles, for his valuable help.

The Author wishes to thank Messrs. Baird & Tatlock for so kindly providing the blocks for the illustrations.

EGERTON CHARLES GREY.

CAIRO, 1924.

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A Short Table of Atomic Weights

(Approximate values)

Name	Symbol	Atomic Weight	Name	Symbol	Atomic Weight
Aluminium ..	Al	27	Lead	Pb	207
Antimony ..	Sb	120	Lithium ..	Li	7
Arsenic ..	As	75	Magnesium ..	Mg	24
Barium ..	Ba	137	Manganese ..	Mn	55
Bismuth ..	Bi	209	Mercury ..	Hg	200
Boron	B	11	Molybdenum	Mo	96
Bromine ..	Br	80	Nickel ..	Ni	59
Cadmium ..	Cd	112	Nitrogen ..	N	14
Calcium ..	Ca	40	Oxygen ..	O	16
Carbon ..	C	12	Phosphorus ..	P	31
Chlorine ..	Cl	35·5	Platinum ..	Pt	195
Chromium ..	Cr	52	Potassium ..	K	39
Cobalt ..	Co	59	Silicon ..	Si	28
Copper ..	Cu	63·5	Silver	Ag	108
Fluorine ..	F	19	Sodium ..	Na	23
Gold	Au	197	Strontium ..	Sr	87
Hydrogen ..	H	1	Sulphur ..	S	32
Iodine	I	127	Tin	Sn	118
Iron	Fe	56	Zinc	Zn	65

Micro Methods in Practical Chemistry

INTRODUCTION

The microscope and pocket lens

For micro chemical work every student should be provided with a pocket lens, and he should be given frequent opportunities of looking at specimens under tne microscope. The form of crystals, the nature of colloidal solutions and emulsions, the appearance of natural products, the changes which take place during precipitation and solution, offer admirable subjects for demonstration.

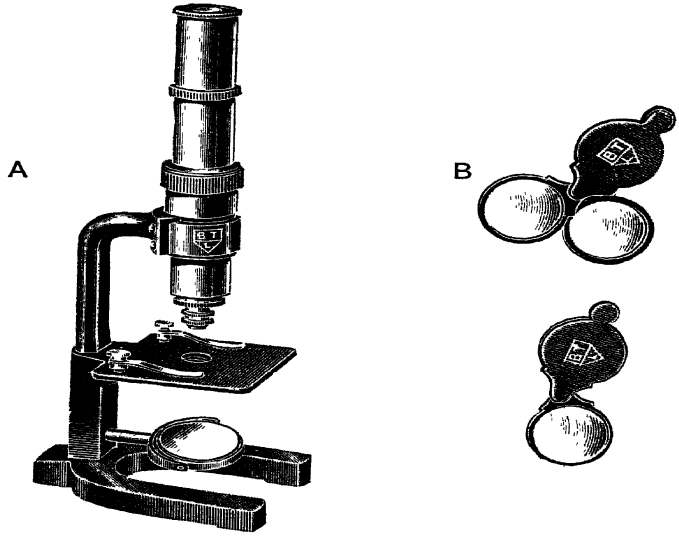


Fig. 1.
A. Microscope for demonstrations. B. Forms of pocket lens for general use.

The equipment of the laboratory

For work with the small type of apparatus laboratory benches need not be elaborate ; in fact simple tables would do. Sinks and water taps and other fittings may be reduced to quite small

dimensions. The apparatus is so compact that it may be kept in a small cupboard or in a box which can be issued with a number to each student. By such an arrangement may students many in turn work at the same bench.

Shelves upon benches are not necessary, and if present they should be small, thus enabling students while seated at work to watch any demonstrations carried out by the teacher, and the practical classroom and lecture room can in this way be combined, which means a gain of space.

Reagent bottles may be conveniently supported in racks of the type shown in Fig. 2.

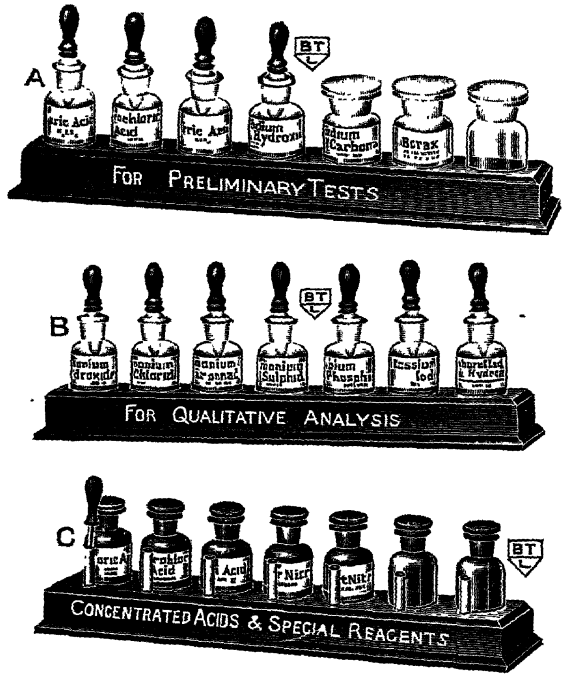


Fig. 2. Reagents and Reagent Bottles.

A. A set of six reagent bottles for preliminary tests, with a space left for one optional reagent. Bottles, 1 ounce capacity.
B. A set of seven reagents for systematic qualitative analysis. Bottles, 1 ounce capacity.
C. A set of three concentrated acids, two special reagents, and spaces for two other special reagents. Bottles of coloured glass. Bottles, ½ ounce capacity.

Such racks are easily made out of blocks of wood. In the figure three racks are shown : (A) for preliminary tests, (B) for systematic qualitative analysis, and (C) a set of smaller bottles of coloured

glass for concentrated reagents and certain special reagents such as silver nitrate. For dilute reagents the bottles are fitted with dropping pipettes, but for concentrated reagents stoppered bottles are recommended. These may be obtained with glass rods attached to stoppers, or a small pointed glass rod may be kept in a strong glass tube near the bottle in a special space provided in the rack; this arrangement keeps the rod clean. By using a rod it is not possible to remove more than one drop of concentrated acid at a time. With coloured bottles for concentrated reagents the danger of confusing them with the dilute reagents is obviated.

Dilute reagents should be of definite concentration. One reason why a student often uses so much material is that in the laboratory solutions are not of equivalent strength, and he has no idea as to the quantity with which he is dealing. It is therefore a great advantage to make up solutions at least approximately equivalent. A convenient dilution is decinormal for precipitating reagents, and normal for solvents. Should the student require a decinormal solvent it is easy for him to take one drop of the normal and add to it nine drops of water.

Working in this way impresses on the student the quantitative idea from the start. An ounce contains about five hundred drops and this should therefore suffice for five hundred tests.

Economy in heating

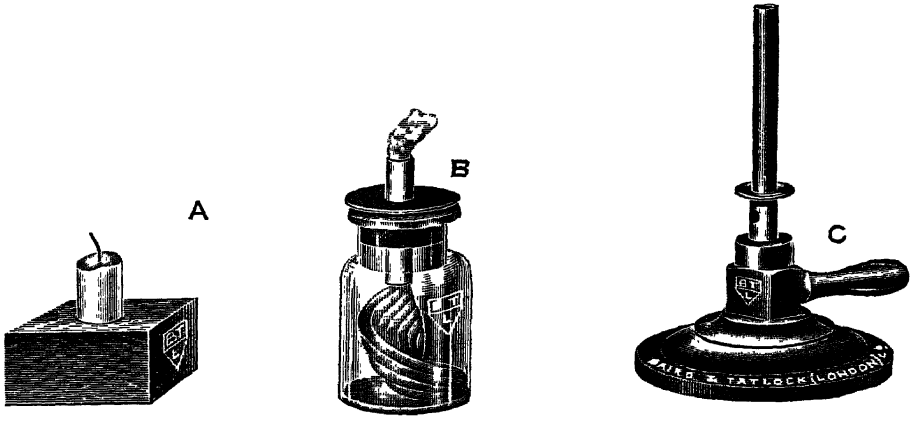


Fig. 3. Economic Sources of Heat.
A. Candle supported in block of wood.
B. Ink bottle turned into a spirit lamp.
C. The micro Bunsen burner.

Making micro apparatus

The student will find it an advantage to make some of the apparatus himself. Micro pipettes and small tubes are readily made from soft glass tubing (see Fig. 7).

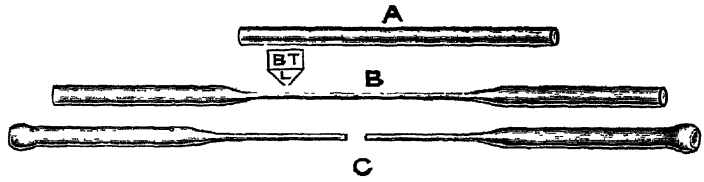


Fig. 7. Stages in making pipettes.

A. The original piece of tubing
B. The tube heated at the centre and drawn out.
C. Two pipettes with broad ends, round in the flame.

Many other pieces of apparatus may be economically made on a small scale, such for example as a generator for hydrogen, sulphuretted hydrogen, or carbon dioxide, and for obvious reasons the small form of apparatus has many advantages.

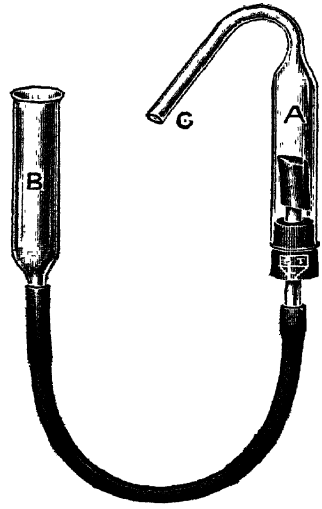


Fig. 8. The micro gas generator for H_2S, CO_2, H_2, etc.

A. Tube holding solid.
B. Tube holding acid solution.
C. Delivery tube for gas.

CHAPTER I

Physical Properties of Metals

Section 1.

Examine systematically the metallic elements supplied to you. Record your observations in the form of tables.

Note with regard to each metal the following points.

(*a*) **Appearance.**

(i) *With the naked eye.* Note the colour, lustre, crystallinity, etc.

(ii) *With a lens.* Examine the surface of the metal carefully. Describe the appearance.

(*b*) **Hardness.**

The hardness of a substance is judged by its capability of scratching other substances or being scratched by them.

Try the effect of the finger nail on each of the metals. Notice if a mark is made, and, if so, whether with ease or not.

Try the effect of a steel pocket knife. Compare the marks made and the ease with which they are made.

Draw up a table in your note-book arranging the metals in their order of hardness, commencing with the hardest metal.

(*c*) **Streak on paper.**

Try to make marks on paper with each of the metals. Note those metals which make a mark and the colour of the mark.

(*d*) **Malleability and brittleness.**

By malleability is meant the capability of being beaten out into thin sheets. Brittleness is the opposite, and can be called the capability of being suddenly broken.

Take a small piece of each metal and try to crush or flatten it on a piece of paper with your pocket knife.

(*e*) **Specific gravity.**

This is a property which is constantly of service to the chemist, and it is therefore important that the student should practice the various ways of determining it.

The specific gravity of a substance is the ratio of the weight of any given volume to the weignt of the same volume of water.

Weigh a piece of metal ; ascertain the number of ccs. of water it displaces when dropped into a small graduated tube. The weight in grams divided by the volume displaced in ccs. gives the specific gravity of the metal.

(*f*) **Melting point.**

This is again a valuable criterion in recognising a substance. Each pure substance has its own melting point. With the metals this point is generally high, an exception being mercury.

(i) Hold minute fragments of, say, two different metals on a knife blade in the candle flame. If they do not melt try a hotter flame. Observe which metal melts first.

(ii) Examine the fragments of alloys and other minerals supplied, and state approximately their melting points, comparing them to the melting points of the metals you know.

A table of melting points is given at the end of the book. (See p. 118.)

CHAPTER II

Experiments with Flames and Burners

The Use of the Blow-pipe

2. Different kinds of flames

(*a*) Strike a match and examine the flame carefully. Try to describe in your own words of what the flame consists.

Is the flame a material thing, and, if so, what is the state of the matter? Is it a gas, and if you think it is, explain why you think so.

(*b*) Turn on the gas and light your gas burner. Notice that you can obtain two kinds of flames, one luminous like the match flame and the other non-luminous.

(*c*) Examine the burner, carefully unscrewing the parts. Before putting the parts together clean them very carefully with a little oil or grease.

(*d*) Draw diagrams of the various parts of the Bunsen burner, showing how the gas and air are mixed, and how the proportions of the mixture are regulated.

(*e*) Draw diagrams of the different kinds of flames you can obtain with this burner and describe the various parts of these flames, comparing them to the match flame and to any other flames which you have examined.

(*f*) Before screwing back the large tube of the Bunsen burner apply a light to the pin hole jet. Notice carefully the kind of flame.

Is the flame luminous or non-luminous? Why is it so high and so narrow? Why is it cylindrical in form? Why are flames pointed at the upper end?

(*g*) Turn the gas tap so as to make a very small flame. See how small you can make your flame without allowing it to become extinguished.

Luminous flames contain either free carbon or compounds of carbon which are on the point of decomposition yielding free carbon.

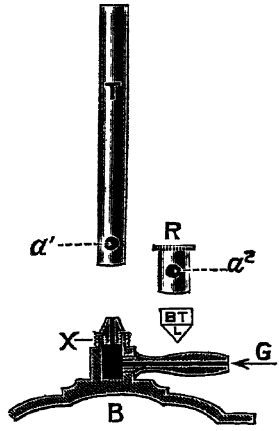


Fig. 9. The parts of the Bunsen burner.

T. Tube which screws on to the base.
B. Base with projection x on which the tube is screwed.
G. Tube through which gas enters. There is a pin-hole exit at X.
R. Ring which can rotate around the base of the tube T.
a^1 Opening at base of tube.
a^2 Opening in the ring.
The supply of air is regulated by means of the ring R.

(*h*) Prove the above statement by holding a cold white plate in the flame. Notice the deposit of the black material, carbon. This variety of carbon we call lamp black.

Besides carbon the coal gas contains hydrogen. During combustion hydrogen combines with the oxygen of the air to form water.

Prove the above statement by observing the formation of a film of moisture on a cold plate held above the flame.

3. The structure of the flame

There are three main parts to a flame.

(*a*) An innermost part where there is no combustion.

(*b*) A middle part where there is partial combustion.

(*c*) An outer part where combustion is complete.

Prove these statements by pushing a piece of wood quickly into a flame. You will see charred lines separated by a space which is not charred at all.

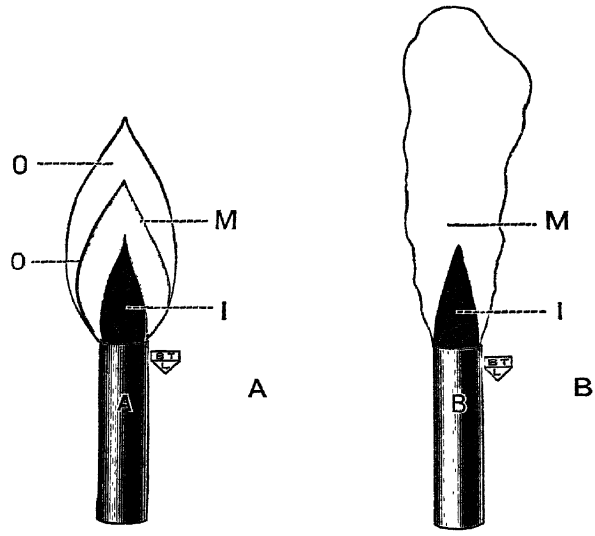


Fig. 10. Flames.

A. *Non-luminous flame.*
O. Outer zone of complete combustion (hot area of flame).
M. Middle zone of partial combustion.
I. Inner zone (cold area of flame, no combustion).

B. *Luminous flame.*
M. Large area of imperfect combustion (cooler than the M of the non-luminous flame).
I. Inner zone (no combustion).

4. The reducing flame

The middle part clearly requires more oxygen to convert it into the non-luminous state of the outer part, and since it requires more oxygen it is able to remove oxygen from materials which contain it. For this reason it is called the **reducing part of the flame.**

For many purposes, as, for example, in the smelting of metallic ores, to get the metals, we require **a reducing flame.** We therefore arrange a flame so that the inner part is the largest. You will see how to do this by the use of the blow-pipe.

5. The oxidising flame

The outer part of the flame is a region of great heat, and contains excess of oxygen for it is nearest to the air. There are no longer unburned gases to take away the oxygen so that there is oxygen to spare for any substance capable of combining with it. This, then, is clearly **the oxidising part of the flame.**

By arranging a flame so that the oxidising region is large we obtain **an oxidising flame.**

6. The blow-pipe

Examine carefully the long metallic tube which we call a blow-pipe. If it is made in parts, take it to pieces, clean it, and put it together again after noting carefully the form and purpose of each part.

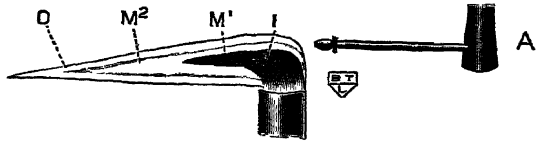
The blow-pipe has three purposes.

(*a*) To direct a flame where we will.

(*b*) To increase the supply of air (oxygen) as desired so as to obtain more rapid combustion, and hence greater heating.

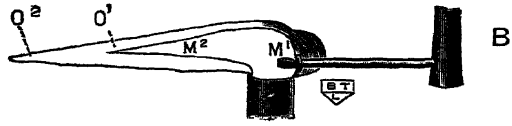
(*c*) To obtain a flame containing excess of oxygen for purposes of oxidation.

Fig. 11. Blow-pipe flames.



A. *The reducing flame.*

O. Small outermost area, oxidising to be avoided.
M^1M^2. Large blue middle zone. The tip M^2 is the hottest portion of the reducing flame, and is to be used for reduction.
I. Innermost area; cold; not to be used.



B. *The oxidising flame.*

O^1O^2. Large outermost oxidising area, O^2. The tip is extremely hot, and is to be used for oxidation.
M^1M^2. Middle blue area of partial combustion.
I. Absent.

7. Making the blow-pipe flames

Try to think out for yourself how you could make a good reducing or a good oxidising flame. Practice using the blow-pipe. Try first by yourself; then read carefully the following notes and see where you were wrong or incomplete in your ideas.

If you have thought rightly you will have decided that for the

reducing blow-pipe flame you must not blow too much air into the flame, and therefore it is best to put the tip of the blow-pipe just near the side of the flame. The air will blow the flame as a whole in the direction you require, but will not pass into the inner zone, which will consequently remain a large reducing area. This central zone will be hotter than the ordinary luminous flame because some oxygen diffuses into it, but it never becomes an oxidising flame. (See Fig. 11 (*a*).)

Note carefully that there is a small outer oxidising zone and material placed in this zone will oxidise. The object has been gained, however, by making the main portion of the flame an area of reduction.

In order to use the flame to the best advantage, a material which is to be reduced must be plunged into the inner part of the reducing flame and not right at the tip, for here there must be oxidation. The tip of the blue inner cone is the best point for a combination of heat with absence of oxygen.

On the other hand, in order to make **the oxidising blow-pipe flame,** since we need to mix the air and the burning gases thoroughly, we place the tip of the blow-pipe well into the flame, and blow the air through the centre of the flame. Materials to be oxidised will be placed at the extreme tip of the flame some distance beyond the tip of the blue cone. (See Fig. 11 (*b*).)

We have noted above, three reasons for using the blow-pipe. The student should now write down in his book which of these reasons comes into consideration in connection with the reducing and oxidising blow-pipe flames respectively. The question must be answered by a study of the flames, not by theory.

Is it only for the first reason given above that the blow-pipe is employed to create the reducing flame? Write down your answer.

How could you make a better oxidising flame than by blowing into it as you are doing?

Further notes on the art of using the blow-pipe

8. The choice of a suitable flame

Use only a small flame. In many ways a candle flame is better than a Bunsen flame. Either may be used for these exercises. The flame of a small spirit lamp is also convenient.

An important use of the blow-pipe is in prospecting for metals. Gas may not be available, and a candle or spirit lamp flame is then of great value.

The use of the blow-pipe is an art not easily acquired, but very useful when learned. Practice hard to gain the mastery of it. By this art you can quickly tell whether a stone contains useful metals such as silver, copper, lead, tin.

9. The choice of a support for the substance to be heated

In starting blow-pipe work seat yourself comfortably at the bench, leaning upon your elbows. Your hands should feel quite free from all strain. Hold the blow-pipe in the right hand, grasping it low down near the sharp bend or angle. Hold the support for the substance to be heated in the left hand.

The support may be a charcoal block, or a piece of pipe clay, or small piece of asbestos, or fire brick. Graphite is also useful, and many experiments may be done by using the tip of a lead pencil to support the material to be examined. We shall use this method a good deal when we come to study the various colours imparted to flames by substances.

Another useful support for blow-pipe work is a piece of platinum, for this material does not burn away. Unfortunately platinum is very expensive. The material to be heated is held in a loop of platinum wire much like the eye of a needle. We shall consider this method later.

10. The control of breathing during blow-piping

You must breath all the while with the cheeks and tongue, not with the chest. This is easily done with practice. Try puffing out the cheeks and holding the mouth full of air. Let the air out slowly between the half-closed lips, and take in more air through the nose before the mouth is empty of air. You will soon find that you can keep up a steady blowing of air from the lips, without allowing the cheeks to collapse.

Practice blowing in this way gently through the blow-pipe. If you allow the tip of the blow-pipe to play against the flame you will soon see whether you are blowing steadily or not.

When you can produce a steady flame in this way practice making the two kinds of flames described above, namely, the reducing flame and the oxidising flame.

CHAPTER III

Analysis by the Blow-pipe

11. Oxidation of metallic lead and tin

(*a*) Make a hole in the charcoal block, about the size of a pin's head, and insert into it a piece of metallic lead. Allow an oxidising flame to play gently on to the lead.

Note carefully the results, in your book, observing whether the metal melts easily, whether a scum is formed, whether there are any colour changes, and so on. Satisfy yourself that you can explain all these changes in terms of the interaction of the metal with the air.

12. Reduction of the oxide to the metal

(*b*) Having oxidised the lead in the manner described above, now try to recover the lead by using the reducing flame. If you do not find this an easy matter, think out the reason for the difficulties. Write down in your book why you imagine it is difficult to regain the bead of lead, although it was so easy to oxidise it. This should lead you to find a way of improving your method of reduction.

(*c*) Repeat the reduction starting with a speck of lead oxide (PbO) or $Pb_3 O_4$.

If you succeed in obtaining a metallic bead, remove it carefully with the point of your pen knife, and examine its physical properties as you did in Chapter I., so as to satisfy yourself that it is lead.

13. Reduction with the aid of a flux

You will have realised that one of the difficulties in bringing about reduction is that many of the conditions which favour reduction, for example, the high temperature, also favour the reverse process.

To prevent the reversal of the change, i.e. from reduction to oxidation, we need to adopt some means by which the lead oxide, as fast as it is reduced to metallic lead, is removed from the surface where it would come into contact with the air. We do this by

employing a flux, i.e. a material which readily melts, and into which the metallic particles can sink, and in which, consequently, they are protected from the air. The metallic particles, sinking in the flux, are able to run together and form into a metallic bead at the bottom of the cavity in the charcoal.

Suitable materials for a flux are sodium carbonate, or a mixture of sodium and potassium carbonates, or sodium borate (borax). As a rule a flux is alkaline, as in the cases mentioned, so that any acid radicle which may be present in the material to be reduced is neutralised.

(*d*) Repeat the experiments upon the reduction of lead and tin oxides, using sodium carbonate as a flux. Take about four times as much carbonate as you take of the oxide.

14. Reduction of oxides of some other metals (copper, iron)

(*e*) Try to reduce some other metallic oxides, for example, copper oxide CuO, iron oxide Fe_2O_3. Make careful note of the result in each case and try to prove whether you have formed the metals.

Where a metallic bead cannot be obtained, it may still be possible to recognise the metal by the appearance. This is the case with copper, and in the case of iron, if the residue after reduction by the blow-pipe be carefully spread out on a piece of paper, and gently crushed to a powder, the metallic particles may be picked out by bringing a magnet near the surface of the powder.

Particles of metal are often more readily discerned if the residue, after blow-piping, is rubbed with a drop of water on a glass slide or in a small mortar.

15. Blow-pipe tests for metallic oxides which cannot be reduced on charcoal

Certain oxides which cannot be reduced by the above method, such, for example, as those of aluminium, zinc, and magnesium, may be recognised by their property of combining with the metal cobalt to form double compounds which have remarkable and characteristic colours. The test is carried out by moistening the oxide of any of the above-mentioned metals with a drop of a solution of cobaltic nitrate, and then heating strongly with the blow-pipe flame. Under these conditions aluminium oxide or other **aluminium** compound give a blue, **zinc** compounds a green, and **magnesium** compounds a pink residue.

(*f*) Endeavour to obtain the coloured residues described above, using one or more compounds of each of the metals, aluminium, zinc, and magnesium.

CHAPTER IV

Recognition of Elements by the Flame Test

16. Principle underlying the test

Absorption and radiation of energy

When substances are heated the particles move, and outward movement is the least restricted. The material becomes in this way looser, and there is an increase in the volume called **expansion.** At a certain point called the **melting point** the particles are so free to move that the substance becomes a liquid. If more energy is put into the substance the particles move still more, and finally escape from the surface of the liquid as gas. This is called **volatilisation** or **vaporisation.** When the particles collide there is an energy exchange, and in this way energy travels through matter by **conduction.** But some energy escapes and is able to act on matter at a distance. This energy is called radiant energy. The process is radiation.

When the particles are moving slowly the energy is represented by the movements of the particles as a whole, and most of the energy can be conducted away, but when the energy present is great, it is represented largely by the vibration of the particles, and under these circumstances a greater proportion escapes as radiant energy.

When the radiant energy is small it may not be apparent, though it may be detected by delicate instruments, but as it increases it becomes evident to our senses, first as heat, and then as light. The kind of light depends upon the kind of vibrations of the particles of the substance. Just as the string of a musical instrument, vibrates in a manner dependent on its form, so do the particles of matter, and as they vibrate they give wave impulses to the medium around them. The slower, longer, wave impulses we recognise as radiant heat, and the faster, shorter wave impulses as light. The slowest of the light impulses are the red ; the fastest are the violet.

Different kinds of light

We have said that the more strongly we heat a substance the more rapid will be the vibrations and the greater proportionally will be the escape of radiant energy, but the nature of the light given out will depend upon the substance. Most complex substances give out white light because the particles vibrate at so many different rates that the various colours blend into one. But elementary substances vibrate in special ways, and may give light of one rate of vibration only ; hence they emit energy which gives rise to the sensation of a single colour. They are said to give monochromatic light.

If, then, we introduce various elements into a non-luminous flame we are able to recognise them by the colour they impart to it. This we call the flame test.

17. The practice of the flame test

(*a*) Hold a piece of wood or paper in the non-luminous flame and observe that white light is emited.

(*b*) Blow some dust into the flame and observe that on the whole the flame emits a yellow light. This is due to the predominance of the monochromatic light, yellow, which is emitted by the element sodium. Sodium is the metal present in common salt which is so abundant everywhere.

(*c*) Hold a copper wire in the flame. Note the difference between the flame with a clean and a dirty copper wire.

Try the same experiment with a steel or iron wire.

(*d*) Place one minute drop of dilute hydrochloric acid on a glass slide, and hold the tip of the copper wire in the drop. Now repeat the flame test and note the difference. Try the same test with the iron wire.

After the tip of the copper wire has rested some time in the drop of acid, dip the point of a splinter of wood into the drop and try a flame test. Does the wood give a colour to the flame.

(*e*) Repeat the experiments with a minute drop of nitric acid.

(*f*) Repeat the experiments with a drop of sulphuric acid.

(*g*) Using a wooden splinter, determine whether a drop of acid colours the flame.

Write down carefully your conclusions from these experiments, and especially answer the following questions :—

(i) Which acid is most convenient for this work, and why?

(ii) Why must a fresh drop of acid be used for each test?

(iii) Why in the latter part of experiments (*d*) did the wooden splinter impart a green or blue colour to the flame, or why does this test succeed even better in experiment (*e*)?

(iv) Does the acid alone colour the flame?

(v) Can you suggest a better support than a wooden splinter for conveying the substance to the flame?

18. Better ways of carrying out the flame test

(*h*) Sharpen a lead pencil so as to have a long, strong, piece of black lead exposed. Black lead is a form of carbon known as graphite. This form of carbon does not readily burn because the particles are so tightly pressed together that the air cannot get at them.

Using the point of the black lead as a support, convey a minute speck of common salt to the non-luminous part of the flame. Note the intense yellow.

Repeat the test with the drop of acid in which you have dipped a copper wire.

(*i*) Repeat these experiments, using as a support a thin, strong fibre of asbestos, instead of the graphite.

(*j*) Repeat the above experiments, using a platinum wire.

Write down what are the advantages and what are the disadvantages for the flame test of a platinum wire.

19. Flame tests with the chlorides of various elements

If the chloride is not supplied the material to be tested may be moistened with a minute drop of strong hydrochloric acid before being conveyed to the flame.

(*k*) Carry out the flame test with the following substances: NaCl, KCl, $LiCl_2$, $BaCl_2$, $SrCl_2$, NH_4Cl, CuO, ZnO, Fe_2O_3, Al_2O_3, MgO.

Make careful note of those elements which you can certainly recognise by the flame test.

Can you think of any still better way by which the flame test can be carried out? How, for example, could you detect barium when copper is present, or potassium when ammonium is present? In general, how could you carry out the flame test when two or more metals were present at the same time?

CHAPTER V

Detection of Metals by Reduction and Oxidation

You will probably have discovered many disadvantages in using a charcoal block for blow-pipe work. It is difficult to work cleanly, and, owing to the absorption of materials by the charcoal, much is wasted.

20. The micro charcoal block or match test

One way in which reduction on charcoal may be made a cleaner and less wasteful process is by the use of a very minute charcoal block, in point of fact the end of a charred splinter of wood. If you char the end of a match stick and impregnate the charred end with sodium carbonate, you have all the requisite conditions for reduction when the charred end is again held in the reducing flame. It is best to use a candle flame or the luminous flame of a Bunsen burner.

(*a*) **To prepare the charred match stick** proceed as follows: Char the point. Touch it with a drop of water. Rub it on a crystal of sodium carbonate, or dust on it a few specks of the powdered anhydrous sodium carbonate. Reheat till the point is again dry.

(*b*) **To carry out the test,** dust a few specks of the unknown material to be examined upon the charred match end, and heat in the candle or luminous Bunsen flame till the material has sunk well into the impregnated charcoal, and the whole has been seen to glow.

(*c*) **To examine the products of reduction,** break off the charred end of the match wood, and grind it gently on a microscopic glass slide, or in a porcelain or glass vessel or, failing this, upon a piece of glazed white paper. Try whether any of the powder is attracted to a magnet. If some particles jump up to the magnet they probably contain **iron,** possibly **cobalt** or **nickel.**

Other metallic particles such as **copper** or **silver** or **lead** may be recognised, especially if the powder be rubbed with a drop of water and examined with the pocket lens or microscope.

(*d*) Practice the above method, using the oxide or some salt of some known metal such as iron, copper, lead, silver, bismuth, tin, or cobalt.

(*e*) Try to identify by the above test various oxides or salts.

21. The Borax bead. Theory

But although we have in a measure overcome some of the objections to the charcoal block by the use of a minute charred rod there remain still others, for example, amongst the charcoal it is difficult to see dark coloured particles such as of iron or some of the oxides of metals. Moreover, we may require to work with a very minute amount of material, as much, for example, as would be covered by the head of a small pin, and we do not wish, therefore, to mix this minute speck with charcoal where it would be difficult to see.

It may therefore have occurred to you that for many purposes a white background would be more suitable. This result can be achieved by using the white substance borax as the supporting material in which to carry out either the reduction or oxidation. Borax is a material somewhat analogous to glass, in chemical composition, and it fuses to a glass-like mass. It is itself not changed when heated in presence of excess of oxygen, nor does it lose oxygen ; it may consequently quite well be submitted to the action of the oxidising or reducing blow-pipe flames. Any substance mixed with the borax which is altered by reduction or oxidation would show these changes well against the white background of the borax ; moreover, borax is an alkali, and has the property of combining with acid oxides to form salts, and since many of these are coloured they are readily recognised.

In practice we use only a small amount of borax which we take up on the end of a platinum wire, and melt in the flame so that it forms a small bead. It is generally found most convenient to turn the end of the platinum wire into a loop.

22. Practice

Take up a little borax on the loop, melt it, and withdraw it from the flame, then, while the bead is still warm, drop on to it a minute speck of the substance to be examined. It is most important that the amount of material for examination should be minute compared to the size of the borax bead, indeed only a microscopic amount is required. The borax bead is then re-heated, either in the reducing or in the oxidising flame, and all the changes which the substance undergoes are most carefully noted. For this purpose a pocket lens or other form of microscope is of great value.

In the absence of a platinum wire, a thin rod of baked clay such as is used for the support of an incandescent burner may be employed. The student will probably like to try other materials such as a thin glass rod or tube. (Soft glass is best, i e. glass of low melting point.)

A fine rod of asbestos or pointed piece of porcelain may also be used.

Practice making the borax bead either upon a loop of platinum wire or with one or more of the alternative supports suggested above, and carry out the following tests :—

(*a*) Observe the effect of heating a minute grain of sand in the oxidising and reducing flames. Is there any effect? How do you explain the changes? Repeat the experiment, using a minute fragment of glass instead of sand.

(*b*) Using minute specks of material, examine successively the series of oxides or salts which you used in Practice No. 1 of this chapter. Note the effect in each case of the reducing and the oxidising flames. Pay particular attention to the appearances obtained with iron, cobalt, manganese, copper and chromium.

(*c*) Repeat the above test, using minute particles of the metals themselves. Can the metals be oxidised in the borax bead?

Observe carefully each stage of the changes which the above substances undergo, using your pocket lens.

How would you classify the various changes which you have observed?

(*d*) What is the effect of heating organic materials such as sugar or starch in the borax bead? Try these experiments and write down your conclusions. Use only a minute amount of material and examine most carefully the appearance of the borax bead under the lens. What new phenomenon do you observe?

Changes observed in a borax bead

	Oxidising flame		Reducing flame	
	Hot	**Cold**	**Hot**	**Cold**
Copper	Green	Blue-green	Colourless	Brown-red
Iron	Yellow or dark red	Yellow-green	Green	Emerald green
Manganese	Amethyst	Red-violet	Colourless	Colourless
Cobalt	Blue	Blue	Blue	Blue
Nickel	Violet	Red-brown	Grey	Grey

CHAPTER VI

Further Experiments of the Effect of Heat

23. Theory

A further disadvantage associated with the charcoal block as a support when heating substances is that many changes of necessity escape unnoticed, for example, if a gas such as carbon dioxide were evolved by the decomposition of the substance under examination it could not be distinguished from the carbon dioxide produced by the combustion of the charcoal, and the same remark applies to carbon monoxide. Again, water vapour becomes so hot in the neighbourhood of the heated charcoal that it is invisible, and therefore we do not detect any water derived from decomposition of a substance containing water, or from the combustion of substances containing hydrogen. For rather similar reasons we often fail to detect other gases with certainty, for example, sulphur dioxide, nitrogen peroxide, the halogens, chlorine, bromine and iodine, or acids derived from these substances such as sulphurous, sulphuric, hydrochloric, nitric acid, etc. And not only non-metallic compound or elements may escape our notice, but also metallic elements and compounds if these are volatile, for example, compounds of mercury, arsenic, zinc, cadmium, tellurium, and so on.

We are led, then, clearly to adopt methods whereby these volatile substances may be collected and examined.

It will have been evident also that in blow-pipe work we have difficulty in excluding the air, which not only dissipates the products, making them sometimes difficult to detect, but also makes it difficult to avoid some oxidation. Many oxidation products are characteristic and easy to detect, but if the oxidation is rapid we may miss many of the stages which would have given a clue to the nature of the substance. For example, many substances give carbon monoxide on decomposition, others give the same substances on being heated with insufficient air to form the dioxide, but under the conditions of the blow-pipe work this gas would rapidly oxidise to carbon dioxide, and we should not be aware that it had been formed.

To gain more detailed information as to the effect of heat on substances, therefore we need to arrange for the following conditions.

(i) That the substance can be gradually heated, the temperature being well under control. We may be able to watch in this way the stages of decomposition.

(ii) That the vapours evolved in the decomposition may be collected by condensation on a cool surface, and that the gases evolved may be collected or examined during their evolution.

(iii) That the supply of air to the substance being heated may be under control.

All these desiderata may be gained by carrying out the heating in tubes of various form.

24. Practice. Choice of the tube for heating the substance

If we desire to reduce the amount of air present to a minimum, we use a tube closed at the bottom. Such a tube is referred to as a closed tube. But if we require that the substance should be heated in a current of air we bend the tube at the bottom so that the substance to be examined may be prevented from falling out of the tube, and then hold the tube, with the long limb pointing upwards, so that it shall act as a chimney and carry the escaping fumes upwards, where they may be condensed. Such a tube is referred to as an open tube. With either form of tube should it be of importance to collect any vapours which arise from the heating of the material, it may be found an advantage to bend down the long limb, this would prevent the condensed liquid running back into the hot part of the tube.

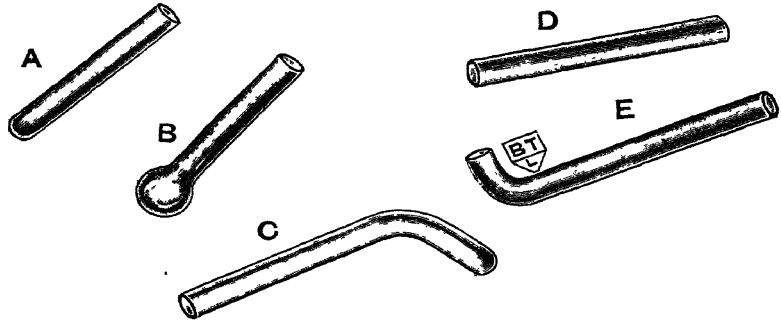


Fig. 12. Tubes for the study of the effect of heat.

A. Simple closed form.
B. Closed tube with bulb.
C. Closed tube with long limb bent down to prevent the return of condensed liquid to the heated portion of the tube.
D. Simple open tube.
E. Open tube with bend.

25. Detection of the decomposition products

(*a*) **Note the physical changes** at all stages of the heating. This gives indirect evidence as to the composition of the substance. Observe melting, crackling (called decrepitation), discolouring, sublimation, distillation or vapourisation.

(*b*) **Examine the gas** in the tube or issuing from it. Is it inflammable (does it ignite at the mouth of the tube)? Does it support combustion (does it rekindle a glowing splinter)? Has it a recognisable odour? Is it alkaline or acid? (Observe action on litmus paper.) Are halogens present? (Observe action on potassium iodide and starch paper.) Is carbon dioxide present? (Observe action on a drop of lime water.) Is the gas a reducing agent? (Observe action on a drop of iodine solution.)

The five last named important tests may be carried out rapidly as follows : Upon a glass slide place one or more drops of the following solutions : iodine, neutral litmus,* lime water, potassium iodide and starch, and silver nitrate. Allow the vapours escaping from the tube to play in turn on each of these drops.

(i) Decolorisation of iodine indicates a reducing agent, probably sulphurous acid.

(ii) Change of colour of the litmus indicates acid or alkali.

(iii) Cloudiness in lime water indicates carbon dioxide.

(iv) Blue colour in starch and iodide solution indicates halogens.

(v) Cloudiness in silver nitrate indicates halogen acids.

Litmus paper and potassium iodide starch paper may be used in place of the solutions.

Note on indicators.

* A reagent which by yielding a characteristic colour indicates the presence of another substance is called an indicator. The word is mostly used for such reagents as indicate the presence of acids or alkalies, for example, litmus, phenol phthalein, methyl orange and other dyes.

(*c*) **Examine any liquid which condenses in the tube.**

Note its colour or other physical signs.

Remove the liquid by a fine pipette of capillary tubing, or by a fine roll of filter paper, and examine its reactions as above.

If a capillary pipette is used the condensed liquid may be added drop at a time to each of the reagents described above.

If the roll of filter paper is used, drops of the reagents may be added to the paper, or the paper may be cut into minute fragments and these added to the drops of the reagents on a glass slide as before.

(*d*) **Examine the solid sublimate if any has formed.**

Note carefully what is to be seen with the pocket lens. Is it coloured? Is it metallic? Is it crystalline? Is it dry or wet?

Remove some of the material by means of a wooden splinter or match stick ; dissolve it if possible in a few drops of water and examine it as above.

(*e*) **Examine the solid residue which remains.**

It is important to be sure that the residue cannot be decomposed further or converted into a sublimate or distillate previously examined.

If the residue cannot be decomposed further in the closed tube it may be examined by heating in an open tube as described later, or by heating on charcoal, or in the borax bead as described previously, or by the match test.

26. Systematic studies in the action of heat

A word about method

(i) Begin by applying very gentle heat, and do not raise the temperature until you are satisfied that you have observed all the changes which are occurring at that temperature. Gradually increase the temperature by approaching the tube to the flame, and as soon as some change begins keep the tube in this position until the change is completed before attempting to raise the temperature further. Note very carefully the changes at every stage. At any moment some decomposition may occur which will give the clue to the nature of the substance under examination.

(ii) Have ready all the apparatus or materials which you need for detecting the decomposition products, for example, of reagents, you will need lime water, iodine solution, starch and iodide paper, litmus paper, turmeric paper; and of apparatus, a microscopic glass slide, dropping pipettes for the reagent bottles a piece of porcelain, one or two thin glass rods, a pocket lens, and some filter papers, cut into small strips, wooden splinters to test for oxygen, etc. Remember also an asbestos mat on which to put hot objects.

(iii) Adopt a definite order of testing for decomposition products as, for example, that given in the preceding paragraph.

27. Practice

(*a*) **Using a closed tube,** examine the effect of heat upon some of the following substances.

Crystalline copper sulphate, sodium sulphate, magnesium sulphate, ferrous sulphate, potash alum.

Sodium carbonate, sodium bicarbonate, magnesium carbonate, calcium carbonate, copper carbonate, lead carbonate.

Sodium chloride, calcium chloride, copper chloride, ammonium chloride.

Sodium nitrate, calcium nitrate, lead nitrate, ammonium nitrate.

(*b*) **Using an open tube,** examine the effect of heating in air the following substances.

Metallic zinc, mercury and lead.
Copper sulphide, lead sulphide, calcium sulphide.
Arsenic oxide, ferrous arsenide or copper arsenide.

(*c*) **Using which ever kind of tube you think appropriate,** examine the effect of heat upon some of the following alloys, minerals and organic substances.

Solder, brass, white metal, calcite, dolomite, limestone, sulphur, pyrites, malachite, mispickel, realgar or orpiment, gypsum, alabaster, cinnabar, blende, bone ash, wood, coal, starch, sugar, cellulose.

(*d*) Combine the exercises of this chapter with those of previous chapters and endeavour by a combination of these methods to recognise unknown substances.

CHAPTER VII

Experiments with Acids, Alkalis and Salts

28. The formation of acids and alkalis

(*a*) Ignite a small piece of magnesium and allow the white calx or ash to fall into a porcelain crucible. Add a few drops of water and test the following properties of the solution.

Mix a drop of the solution in turn with a drop of each of the following solutions : (1) neutral litmus, (2) phenolphthalein, and (3) methyl orange. Characteristic colours are produced. In this case indicating the formation of an alkali.

(*b*) Take a minute speck of metallic sodium about the size of a small pin's head. Drop it into a few drops of water in a crucible, and note carefully the nature of the reaction between it and the water.

Test the solution obtained, as in the previous experiment, and note that the behaviour towards indicators is similar, but that the solution of the oxide of sodium is more powerful in its action than that of magnesium. This is indicated by the fact that it colours the indicators more strongly.

(*c*) Observe that lead oxide or zinc oxide do not colour these indicators. Why is this?

(*d*) Compare the above results with those obtained when non-metallic oxides were brought into contact with similar reagents. (See previous chapter.)

The above experiments show that metallic oxides, when they dissolve in water, exhibit certain properties which are opposite to those exhibited by solutions of non-metallic oxides. The former give rise to alkalis, the latter to acids. The two kinds of substances are able to neutralise one another when mixed in suitable proportions, and the result is a salt.

29. The formation of salts from acids and alkalis

(*a*) **Neutralisation of alkali by acid.**

Into a small evaporating dish place about one-tenth of a gram of anhydrous washing soda (sodium carbonate). Add about 20 drops of water, and one drop of methyl orange. Add drop by drop a four per cent. solution of hydrochloric acid, until the yellow colour just changes to pink. At this point the indicator shows that the alkali has been neutralised by the acid. You will find about 2 cc. of acid is required (twenty drops).

(*b*) **Evaporation to obtain the solid salt.**

Place the evaporating dish upon an asbestos square and gently evaporate the solution over the Bunsen flame until a dry residue is obtained. This residue is common salt, or sodium chloride. It has been formed by the union of an acid and an alkali, but it has properties different from either of these classes of substances. Test the properties as follows.

(*c*) **Examination of the salt.**

(i) Observe the physical properties. Note the taste. Examine the appearance of the crystals. What is their shape? How could you obtain larger crystals for examination? Transfer a few specks of the salt to a microscopic glass slide and add a drop of water, warm the drop and allow it to cool. Examine the crystals with the pocket lens or, better, with a more powerful microscope.

(ii) Test the chemical reactions as follows: Add drops of the salt solution to drops of the following reagents: (1) litmus, (2) phenolphthalein, (3) silver nitrate, (4) lead acetate, (5) lime water, and (6) sodium carbonate solutions.

(iii) Introduce a speck of a metal such as zinc or magnesium or iron into a drop of the salt solution. Is there a change?

30. Comparison between salts and acids or alkalies

Compare the results of the tests described in section 29 with the same tests applied to acids or alkalis. For example, add hydrochloric, sulphuric or acetic acids to drops of the above-mentioned reagents and observe the behaviour.

(*a*) Note the appearance with the pocket lens of the drop of sodium carbonate solution when hydrochloric acid is added; a drop of acetic acid when chalk is added, and a drop of sodium chloride solution when either acid is added or an alkaline carbonate is added.

(*b*) Compare the effect seen with the lens when a speck of zinc is introduced into solutions of sodium carbonate, sodium hydroxide, lime water, magnesia, sodium chloride and hydrochloric acid respectively.

31. Ammonia and ammonium compounds. Theory

The compound of hydrogen and nitrogen NH_3 called ammonia unites with water to form an alkali, and with acids to form salts.

$$NH_3 + HCl = NH_4Cl.$$

In solution we find the compound NH_4Cl splits into two parts, NH_4 and Cl, but these parts or radicles are very different from the gases ammonia and chlorine; they are called ions.

Other salts also split in solution into ions. The process is explained later. The NH_4 radicle or ion resembles a metal because NH_4Cl resembles NaCl. Therefore NH_4 is named ammonium in analogy to sodium or potassium.

32. Practice

Carry out the following experiments with ammonia and its compounds.

(*a*) Repeat the experiment upon the formation of a salt described in Section 29.

Make use for this purpose of either ammonium carbonate or ammonium hydroxide.

A four per cent. solution of hydrochloric acid will be approximately equivalent to a four per cent. solution of ammonium hydroxide or to a five per cent. solution of ammonium carbonate.

Weight for weight we require more carbonate than hydroxide to neutralise the same weight of hydrochloric acid. Why is this?

(*b*) Prepare crystals of ammonium chloride and examine their form. Is the form similar or dissimilar from sodium chloride?

Make drawings of both forms of crystals.

(*c*) Compare the solubility in water of these two chlorides?

(*d*) Introduce a minute amount of the ammonium chloride, which you have prepared, into a closed tube and gently heat it over a small flame. What do you observe? Can you now think of a way of separating a mixture of sodium and ammonium chloride? Could this method be used for separating other mixtures?

(*e*) What is the appearance under the lens or microscope of the sublimate of amonium chloride?

(*f*) Introduce a speck of ammonium chloride or some other compound of ammonia into a closed tube, and add one drop of a four per cent. sodium hydroxide solution or of some other alkali of equivalent strength. Warm the tube and allow the vapour from the tube to play against a drop of neutral litmus or methyl orange solution, or against a piece of filter

paper coloured with these materials. Note the change in colour. Why has the ammonia been displaced from the solution by the other alkali?

(*g*) Introduce another speck of ammonium chloride into a closed tube and add a drop of five per cent. sulphuric acid. Heat gently and allow the vapour evolved to play against a glass slide on which are drops of the following solutions, viz., silver nitrate, neutral litmus, neutral methyl orange, and lead acetate.

Note and explain all the changes in these drops.

Why has the hydrochloric acid been displaced from the solution by the other acid?

(*h*) Compare the flame test of ammonium with that of potassium.

CHAPTER VIII

Some Reactions with Water

33. A note about wet and dry tests

In the previous chapter we described a method of testing the vapours arising from the decomposition of materials by allowing them to come into contact with drops of various solutions held upon a glass slide. We shall refer to this method in future as **the hanging drop method**; it is a method which lends itself very conveniently to microscopic analysis. We have also made use of drops of various reagents when testing the properties of the solid sublimate in the experiments which we carried out upon the effect of heat on various compounds. Such drops have all been of solutions of reagents in water. It is customary to refer to such tests as **wet tests**, which is a short and convenient term to employ, and it distinguishes these from tests made by heating on charcoal, or in tubes, or on platinum wire, or borax bead, all of which are called **dry tests.** In a wet test the reagent is a solution in water, but the substance to be tested may be a solid, a liquid, or a gas, or a solution of any of these forms of matter. Since, however, no substances react unless their particles are freely dispersed or dissolved, it is clear that in whatever state the substance to be tested may be when added to the reagent, it must first dissolve, and then react, if it is to react at all. We could think of tests in which some other solvent than water would be employed, for example, spirits of wine (ethyl alcohol), but by far the majority of reactions which we shall study will be those taking place in aqueous solution, and therefore when we do not specify the solvent it must be understood that we are referring to water

34. Water as both solvent and reagent

The simplest example of a wet test is one in which water is not only the solvent or medium for the reaction, but also is the reagent, or, to be more precise, one of the reagents, for a reaction must obviously take place between at least two reagents. We must consider, therefore, first the interaction of substances with water. We have noted in the previous chapter that water reacts with the oxides of non-metals to yield acids, and with the oxides of metals to yield alkalis. This fact can be illustrated by the following experiment.

(*a*) (i) Add a speck of lime or magnesia (1) to wet, (2) to dry litmus paper. What is the difference?

(ii) Add a drop of water to a piece of red litmus paper or white phenolphthalein paper. Bring the paper near a

drop of ammonium hydroxide held on a glass rod. Do not allow the solution of ammonium hydroxide to touch the papers, but merely allow the vapour to act. Note the result.

(iii) Repeat these experiment, using sulphurous acid with litmus or pink phenolphthalein paper.

How do these experiments illustrate the point in question?

(*b*) Take a minute speck of each of the following materials and add in each case one drop of water. Copper sulphate (anhydrous), potassium permanganate, cobalt chloride (anhydrous), chrome alum, iron alum, cupric chloride. Describe what you observe, and explain as far as you can what has taken place. To understand what has taken place the next experiment will help you.

(*c*) Having added a drop of water as directed above, now observe the effect of gently heating the drop on a glass slide or piece of porcelain.

35. One form of reaction with water; hydrate formation

The changes which the various substances mentioned in Section 34 undergo when treated with water cannot all be explained in the same way, and it is to be hoped the student has discovered this fact for himself The salts of copper and cobalt behave similarly, and illustrate one form or reaction with water; copper sulphate yielding one and copper chloride yielding two compounds with water, while cobalt chloride yields also two well-marked compounds with water

We can then explain these changes in terms of the formation of compounds with water, and some of the facts are as follows :—

Copper	Cobalt
The chloride without water is brown. Combined with one molecule of water it is green. Combined with two molecules of water it is blue.	The chloride without water is blue. Combined with one molecule of water it is violet. Combined with two molecules of water it is rose red. Combined with six molecules of water it is dark red.

36. Hydrates and hydroxides

We have seen that the colours of the hydrated salts may be changed as we will within the limits mentioned in either column by either drying the salt (dehydrating) or adding water to it. The combination between the salt and water is evidently a very feeble one.

This remark applies to all the compounds which we call hydrates, i.e. compounds containing water of crystallisation. Such compounds must not be confused with the hydroxides, which are sometimes erroneously called hydrates. Sodium or calcium hydroxide, for example, is not the hydrate of the metal. We shall see later what their true composition is, but we already know this much, namely, that the hydroxides are alkalis, whereas the hydrates referred to above are neutral compounds.

The chemical change by which the green copper salt changes to the blue, or the blue cobalt salt to pink, and vice versa, we call a **reversible change.** This is the principle underlying the use of some forms of **invisible ink.**

37. Reversible and irreversible changes illustrated by invisible ink

(*a*) With a pen dipped in a solution of cobalt chloride or acetate or other cobalt salt, write on a sheet of white or, better, of pink writing paper. Allow the writing to dry. It should be practically invisible. On heating the paper gently over a flame the writing will appear in blue letters. If the paper be now allowed to cool and to become slightly damp the writing will disappear, but will appear on again heating. This, then, is a reversible chemical change.

(*b*) Repeat the above experiment, using a dilute solution of sulphuric acid instead of the solution of a cobalt salt. On drying the writing is invisible, but on heating gently over the flame the writing appears in black characters What is the explanation? Is this also a reversible chemical change?

But the changes which chromium and iron alums undergo when treated with water are quite different to those described for cobalt and copper, so that it is evident that we must look for some other explanation. To find this we must study further the properties of the solvent.

CHAPTER IX

Some Elementary Notions about Solution

Our studies of the action of water on certain substances, such as anhydrous salts and complex salts, have led us to see the necessity of a close study of the phenomenon of solution.

38. Substances do not react unless dissolved

It is an old chemical dictum that substances do not react unless they are dissolved. With a view to criticising this generalisation carry out experiments to confirm or disprove the following statements.

(*a*) A drop of ammonium hydroxide solution when held near a drop of strong hydrochloric acid gives rise to thick fumes, even though the drops do not touch.

(*b*) Gases react even more quickly than liquids. For example, oxygen and hydrogen in suitable proportions react with explosive violence, due to the suddenness of combination, whereas methylated spirits burn quietly with a steady flame.

(*c*) A drop of mercury rubbed with the solid substance, iodine, becomes converted into another substance, iodide of mercury, which now dissolves in water if potassium iodide is added.

(*d*) Metals such as iron, zinc, magnesium, in contact with dilute acids, give rise in many cases to bubbles of gas.

(*e*) If the solid substances, sodium carbonate, arsenious oxide, and charcoal are heated together in a closed tube, a mirror of metallic arsenic is obtained, showing that there has been an interaction.

The reduction of other metallic oxides by carbon is similar to the above. Such reactions appear to be between substances in the solid state.

(*f*) If potassium or sodium nitrate is heated in a closed tube with charcoal or sulphur a violent reaction takes place. Both reagents are in the solid state at ordinary temperature.

(*g*) Consider also the following kinds of changes.

(*a*) When such substances such as lead nitrate, ammonium nitrate, potassium permanganate, ferric sulphate, manganese carbonate, ammonium bromide, potassium iodate or bromate, are heated, very obvious changes occur.

(*b*) When organic substances are heated they generally decompose with the production of various substances. For example, by heating sugar we obtain carbon, water and various tar-like materials and vapours of pungent odour.

(*c*) When water was added to anhydrous salts such as those of copper and cobalt we saw an obvious change, but when the water was removed we saw also a marked change, so that both adding and taking away the solvent caused change.

Having verified each of the above data, write down in each case whether you consider that the phenomena which you observe are consistent or inconsistent with the dictum that substances must dissolve before they react.

39. Definition of the terms used in the law just enunciated (Section 38)

You have been asked to verify a law, and before you can do so you must consider whether you understand what it is you have to verify. In other words you must be sure that you understand the language in which the law is framed. The particular law which we are considering states that substances do not react unless they are dissolved. What do the terms "**react**" and "**dissolved**" mean? The meaning is by no means obvious, in fact you cannot know what the words mean unless you ask, because the words are quite conventional. In physics the word react has a very different meaning to what it has in chemistry. We must therefore ask for a proper definition of the terms used in expressing this law.

By the word reaction we mean a mutual effect caused by substances when brought together, which results in the formation of a third substance different in composition from the reagents.

This definition limits the question into which we are enquiring, for it means that we are no longer concerned with such changes as are mentioned in paragraph *g* of section 38. For the law does not apply to mere actions, but only to reactions. Decompositions are actions without doubt, but they may be brought about by physical means, as by the application of heat. The chemical attraction or influence of a second substance does not come into play in changes of this type, and therefore such are not reactions, and the law does not apply to them. All reactions are of course actions, but the converse is not true. When therefore we are dealing with one substance there can be no question of a reaction.

It now becomes easy to see that when water is brought into contact with copper chloride or cobalt chloride there is true reaction, because there is solution, and a third substance, namely, the hydrate is formed in each case. But

in the reverse change the water plays no part ; we are studying the decomposition of a single substance, namely, the hydrate, in each case, and this kind of change is not a reaction, and therefore lies outside the scope of the law.

We have next to consider what precisely is meant by the word **dissolved.** It is quite clear from experiment (*b*) Section 38, that gases react, and we have already been told that in the gaseous state the particles of matter move even more freely than in the liquid state, and this theory of the movement of gaseous particles, called the **kinetic theory,** seems abundantly verified by all our observations. For we have seen how the gases and vapours issuing from heated tubes diffuse into the surrounding air and become mixed with it, disappearing just as salt or sugar stirred into water disappears from view. Van't Hoff's idea was that substances when they dissolve become like gases. It is certainly clear that we cannot distinguish between the dissolved and the gaseous state. In all these states liquid, vapour, or gas, we have one feature in common, namely, that movement of the particles is free in all directions. And this is in reality what is meant by the term dissolved.

We may therefore restate the law as follows. Substances will not combine chemically unless they are in a condition in which their particles are free to move in all directions.

And we may state that matter is dissolved, in the sense of the dictum we are endeavouring to prove, when it exists under any of the following conditions :

(i) When it is in the state of a gas.

(ii) When it is in the state of a liquid.

(iii) When it is in the mixed state known as a vapour.

(iv) When in the solid state it is exposed at a solid surface provided that the forces of chemical attraction opposes the cohesive force which binds the surface particles.

40. Consideration of the preceding experiments in the light of this law

We may now, in the light of these remarks, reconsider the experiments under the headings (*a*) to (*g*). We see that in (*a*) and (*b*) we are dealing with gases, and these may rightly be classed under the heading of solutions using the word in the sense which is implied in the definition. In (*c*) and (*d*) we have experiments in which one of the reagents is a liquid and the other a solid. In such cases we find that the reaction takes place only at the surface where the reagents come in contact. If we consider the outermost layer of a solid we must realise that the particles are more free to move than those particles which lie within. We must consider that the forces which hold the particles of solid metal together are, at the surface, overcome by the attraction exerted between these and the particles of the non-metallic element, and this is sufficient to give these surface particles the degree of freedom which they require for chemical interaction. Thus the change is quite in harmony with the law. The case of the reduction of metallic oxides by carbon does not differ greatly from the cases described in (*c*) and (*d*), for we observe that it is necessary that the materials should be intimately mixed. When finely divided powders are intimately mixed the particles of the reagents must be in contact over a very great surface.

We have seen that at these surfaces the particles of the reagents must be considered to be in a special condition, they must have at least two degrees of freedom, and the force of attraction towards one another of particles of an opposite kind is sufficient to counterbalance the cohesion of the particles of the same kind so that they become virtually free, and can therefore react.

When a flux such as sodium carbonate is present this material melts, and we have a condition of liquid solution.

In experiment (*f*) the nitrate first melts so that the particles are free to move. The nitrate begins to decompose yielding oxygen gas. In the presence of this gas the carbon or sulphur burns as it would if heated in an atmosphere of oxygen Reaction only takes place at the surface of the carbon or sulphur.

41. Solid solution

We have seen that a solvent may be a gas or a liquid. It is only logical to ask whether the solid state may not also act as a solvent. The answer is in the affirmative. Prove this for yourself by the following experiments.

(*a*) Place a drop of clean mercury upon a clean surface of silver or gold. Rub the mercury over the surface by means of a piece of chamois leather or cloth. The liquid will be found to have disappeared and to have united with the solid. In order to separate the mixture the metal may be heated in the flame when the mercury will be dissipated as vapour and the non-volatile metal will remain. The mercury and silver or gold are intimately united in what is called solid solution. Solid solutions of metals are spoken of as **alloys or amalgams.**

(*b*) Upon a small piece of broken porcelain heat together a speck of lead and of tin. The result is again an alloy, known as solder Compare the melting points of lead, tin, and solder. In what way does this solid solution or alloy differ from a mere mixture? You will probably not be able, without some special device, to determine at what temperature the substances melt, but you can make the comparison in the manner described in Chapter I., Section 1 (*f*).

42. In solid solution chemical reactions do not occur because of the limitations to movement imposed by the solid state

The law enunciated in the previous chapter stated that solution was a *sine qua non* for chemical reaction, but the converse is not implied, nor is it true. All reaction must be proceeded by solution, but the solution must be of the kind in which the particles are free to move and this condition is not fulfilled with solid solutions. This fact may be illustrated by the experiments.

(*a*) With a pair of tongs hold a piece of steel or cast iron in a non-luminous flame. The varieties of iron, known as cast iron and steel, contain carbon and iron carbide in solid solution, yet in the experiment the carbon does not burn, for if it did it would impart luminosity to the flame. But if you dip the object into a drop of acid you will appreciate from the odour of the gas that it is not pure hydrogen which is evolved, but a gas, which by its odour recalls acetylene. Thus combination

between carbon and hydrogen occurs readily enough when the conditions for liquid solution are present, but combination between carbon and oxygen does not occur when the conditions are those of solid solution.

(*b*) Repeat the above experiment, using a piece of calcium carbide instead of steel or cast iron. But instead of dipping a piece of carbide into acid use merely water. This experiment shows very well that with the solid material, although both constituents, carbon and calcium, are capable of combining with oxygen, no combination occurs, or it is at any rate restricted, whereas when the liquid solvent is added, the conditions for interaction supervene. The carbon combines with the hydrogen, and the calcium with the oxygen, to form acetylene and lime respectively. The lime reacts with the water to form the hydrate.

Note.—It is not intended to convey the idea here that calcium carbide is a mere solid solution of calcium in carbon, or vice versa, but the example is useful because it is certain that the chemical union between carbon and calcium is very feeble since water annuls it. Yet dry calcium carbide does not readily combine with oxygen.

This absence of chemical change is due not to absence of chemical affinity, but to the limitations of movement imposed by the solid state.

Before leaving the subject of solid solution the student should realise that crystals containing water of crystallisation are examples also of solid solutions. It is surely a surprising thing that water should be solid at ordinary temperature as it is in these crystals.

CHAPTER X

Solution (continued). Physical, Chemical, and Inert Solvents

43. Inert solvents

We must consider a solvent to be inert when the substance dissolved behaves as if it were in a vacuum. Such is the case when oxygen dissolves in nitrogen, or water vapour dissolves in either. We can prove this by ascertaining the partial pressures of the gases. Each gas behaves as though the other were not there, and therefore we may describe the one as an inert solvent of the other.

Verify these facts as follows :

(*a*) Fill two small tubes with water and invert them over a glass of water in such a way as to prevent the water escaping from the tubes. Half fill the tubes with gas, one with air, and the other with hydrogen or coal gas. This is readily done by pushing a thin rubber or curved glass tube into the tubes containing water and blowing in the gas.

(*b*) Hold the mouth of one tube close to the mouth of the other, and, gently tilting it, allow all the gas to pass into one tube. You will find that the half tube full of gas will add to the volume of the other half tube full, and make a whole tube full. How do you explain what has happened?

When one gram of water is turned into steam the volume of steam produced measures more than one litre. Since the volume has increased a thousand-fold, it follows that the distance between the particles must on an average have increased ten-fold. If there is so much space between the particles of a gas, why does not one gas pass into the other without increasing its volume?

44. Physical and chemical solvents

In the case of liquids there is generally an interaction between solvent and dissolved substance (solute). An exception is where certain gases dissolve in liquids, for example, oxygen in water.

When, however, we come to decide what exactly is the nature of the interaction between solvent and solute we enter upon a very difficult problem. What shall be our criterion as to whether the action of the solvent is chemical or physical?

For the present it will suffice to draw the distinction between physical and chemical solution as follows. If, when the solvent is removed, the solute can be recovered unchanged, the solution has been physical, but if the solute is found to have been altered, then the solution was accompanied by a chemical change. Chemical solution can therefore be simplified by resolving it into two stages, firstly, a chemical combination of the solute with part of the solvent, and, secondly, the true physical solution of this compound in the remainder of the solvent.

Practice in the use of various solvents

Study the following cases of solution, and state whether the process is physical or chemical, giving reasons for your conclusions.

Use a minute speck of solid and one drop of fluid for each test.

(*a*) **Water as the solvent.**

Sodium hydroxide, sodium carbonate, sulphuric acid, cupric sulphate, sodium bisulphate, sodium chloride, chrome alum, ammonium nitrate, calcium carbide, as solute.

(*b*) **Dilute hydrochloric acid** (10%) **as solvent.**

Calcium carbonate, copper hydroxide, magnesium or zinc oxide, metallic zinc or magnesium, metallic iron, calcium or ferrous sulphide, potassium iodide, potassium chlorate, calcium phosphate.

(*c*) **Dilute nitric acid** (10%) **as solvent.**

Ferrous sulphate, potassium bromide, potassium iodide, cuprous oxide, metallic copper, sodium sulphite, calcium phosphate, metallic bismuth, metallic zinc or magnesium.

(*d*) **Concentrated hydrochloric acid as solvent.**

Potassium chlorate, potassium iodide, sodium sulphate, sodium nitrate, ferric oxide, cuprous oxide, metallic iron and zinc, sodium chloride, sodium silicate, sodium borate.

(*e*) **With acetic acid** (20%) **as solvent.**

Calcium phosphate, lead oxide, copper carbonate, sodium silicate, sodium borate.

(*f*) **With ammonium acetate solution** (10%) **as solvent.**

Lead oxide, lead sulphate, sodium bisulphate, sodium hydrogen phosphate.

(*g*) **With a solution of sodium hydroxide** (10%) **as solvent.**

Sodium bicarbonate, sodium hydrogen sulphate, ammonium chloride, copper sulphate, arsenious oxide, mercuric iodide, iodine, stearic acid, arsenious sulphide, cellulose starch, albumen.

(*h*) **With methylated spirits or spirits of wine (ethyl alcohol) as solvent.**

Mercuric chloride, ammonium acetate, stearic acid, olive oil, sodium oleate (castile soap), potassium iodide, iodine, anhydrous copper sulphate, potassium permanganate.

(*i*) **With chloroform as solvent.**

Stearic acid, olive oil, iodine, anhydrous copper sulphate, potassium permanganate.

45. Temperature changes during solution. Theory

Another good criterion of chemical change is the evolution of heat during the act of solution. For when a substance dissolves it is spread over a larger space and its particles have therefore reached the same condition as if they had been forced apart by mechanical action. It would be a contradiction to the law of the conversation of energy if the same condition could be reached, in one case with, and, in the other case, without an expenditure of energy; and we may therefore be certain that when a substance dissolves, work is done upon it by the solvent. But if the solvent gives up its energy to any extent, however small, in bringing about solution, it follows that the temperature of the solvent must fall.

The physical action of the solvent alone must lead to a fall of temperature. Therefore if we observe the contrary, viz., a rise of temperature, we have no alternative but to admit that a chemical reaction has taken place. We must adhere to this conclusion even if we cannot at present isolate the chemical substance which is formed by the reaction. For example, when water was mixed with sulphuric acid or with sodium hydroxide there was in each case a manifest rise of temperature. It is only necessary to mix a drop of water with a similar quantity of either of these substances in order to confirm this statement. Steam will be seen to arise from the drops.

The chemical reactions in these cases are undoubtedly hydrate formations. We have already seen how readily hydrates are decomposed. The hydrate of cupric sulphate loses water slowly even at room temperature, and rapidly at 100° C. Crystals of washing soda lose water still more readily than do those of copper sulphate. It is therefore not difficult to understand that some hydrates cannot be isolated at the ordinary temperature, though they might be obtained by freezing the solution.

In the preceding exercises there have been examples of both physical and chemical solution, and it is to be hoped that the student has been able to distinguish in many cases between the one kind and the other. He must, however, grasp clearly the idea that although physical solution is possible without chemical change, the converse is not possible. Chemical solution, in other words, consists of at least two stages: firstly, chemical interaction, and, secondly, physical solution of the product of the interaction.

The difficulty may, however, arise in the student's mind as to how a true physical solution is to be distinguished from an inert solution. How, for example, can we prove that the solvent actually exerts a physical effect? How, to take a particular case, does water, when it dissolves sugar or salt, act in a manner different from that of air when it dissolves water vapour or carbon dioxide? The answer is, firstly, that physical changes may be observed during the act of solution, and, secondly, that the physical properties of the solution are different from those of the pure solvent. A detailed study of the properties of solutions must be reserved till later, but for the present the student may satisfy himself as to the correctness of the above statement by the following simple experiments.

CHAPTER XI

The Physical Properties of Solutions

46. The lowering of the vapour pressure of a solvent by the addition of a soluble substance

(*a*) Upon a piece of filter paper place two drops, one of pure water, and the other of a strong solution of salt in water. Do not allow the liquids to mix. Allow the wetted paper to dry by moving it in the air or gently warming, and notice that it is the drop of pure water which disappears first. Evaporation depends upon vapour pressure and the solution with the greatest vapour pressure evaporates fastest. The effect of the dissolved salt therefore clearly has been to lower the vapour pressure of the solvent (water).

(*b*) Repeat the experiment, using other salts and other absorbent materials.

(*c*) Repeat the experiment described above in the following way. Into a small glass or porcelain vessel place about 10 cc. of water and bring the water to the boil, turn down the flame until it is only just large enough to maintain the water on the point of boiling. Now add quickly 0·5–1·0 gram of common salt. The solution will cease to boil. If you have controlled the size of the flame with great care you will find that you need to increase it in order to bring the salt solution back to the boiling point. Thus the boiling point of a salt solution is seen to be higher than that of pure water. The salt has raised the boiling point. That substances when they dissolve raise the boiling point of the solvent is only a particular case of the general phenomenon that they lower the vapour pressure.

At a later stage we shall study this important phenomenon in a quantitative manner, but should the student be already in possession of a thermometer registering up to 110° C., he could carry out an interesting experiment to determine the relation between the amount of salt added to water and the extent of the raising of the boiling point. Even an attempt at a quantitative experiment is better than a mere qualitative one.

47. The osmotic pressure of a solution. Theory

The view held by Van't Hoff, that dissolved substances behave as though they were in the gaseous state, has been mentioned, and the student will naturally expect to know upon what facts such a view is based. That the volume occupied by the solute is the volume of the solvent will offer no difficulty, for it is clear that, provided the solution is well stirred, the dissolved substance passes to every part of the liquid, and ultimately reaches a uniform degree of concentration throughout.

The intimacy with which the solute and solvent become mixed is far greater than could be attained by any mechanical mixing of powders. The most powerful microscope or ultra-microscope, fails to reveal any outline of the solid particles which have become dissolved, and we have therefore no alternative but to consider that they are reduced to the finest degree of division possible, namely, to the molecular state. The solid particles, therefore, move about in a solution by a process of diffusion in a manner analogous to the particles of a gas. Diffusion is, however, very much slower with solids in solution than with gases dissolved in other gases, because in the liquid solution the particles of the solvent are so close to one another that they offer a real resistance to the passage of other particles between them, whereas in the gaseous state, as we have seen, the solvent molecules are widely separated, and consequently other particles may pass without hindrance amongst them.

That the particles of a dissolved substance should be able to diffuse throughout the solution against mere gravitational force would imply the exertion of a force, but in the case of a liquid solution the force to be overcome is far greater than gravitational attraction ; it is the resistance of the fluid molecules to the passage of other particles amongst them. This resistance is often called viscosity. The dissolved substance must clearly exert a pressure in order to overcome the viscosity of the solvent, for otherwise the dissolved molecules could not diffuse from place to place. This pressure is called the osmotic pressure (from the Greek ὦσμος, meaning a pushing or struggling). The total osmotic pressure of a solution is derived from the united pushing of the dissolved molecules. We know from the study of the mechanics of a fluid that the pressure is the same in all directions, and it is measured by the force exerted in any one direction multiplied by the area over which the force is applied.

We may express the force by comparing it to gravitational force, and speak of so many pounds to the square inch or grams to the square centimetre, meaning the force exerted by gravitational attraction upon a pound or a gram mass respectively over an area of a square foot or centimetre.

Now we have seen that the heat required to vapourise a liquid such as water is very considerable, and this represents the work done in separating the liquid molecules. But when a dissolved substance diffuses through a solvent its particles must force aside the molecules of the solvent just as does heat ; we may therefore be justified in anticipating that the osmotic pressure in a solution must be very high.

Another way of approaching the matter is to recall the simple gas law of Boyle, which tells us that the product of pressure and volume is a constant. But in a solution we have seen the molecules are much closer than in a gas, or, in other words, the volume is less, and consequently the pressure in the solution must be more in order to keep the product PV constant. The osmotic pressure must therefore be high if the osmotic pressure corresponds to the gas pressure, i.e. if the conditions in the solution correspond to those of the gas.

48. Osmotic pressure demonstrated by the swelling of jellies containing sugar. Practice

Make a ten per cent. solution of gelatine as follows :—Soak 10 grams of gelatine in 100 cc. of water in a small glass beaker or other thin walled vessel.

After some hours soaking (the mixture may be left all night) you will observe that the gelatine has greatly swollen. Place the vessel in a larger vessel containing water and heat the water. This procedure enables you to heat the gelatine and water together, at a temperature not exceeding 100° C., until the gelatine has entirely dissolved. When this state is reached pour 3 cc. of the solution of gelatine into each of three separate tubes. Keep the remainder for the later experiments.

Add to No. 1 tube 1·0 cc. distilled water.
2 „ 1·0 cc. saturated sugar solution (syrup).
3 „ 1·0 cc. dextrine solution (gum).

If the jellies in the tubes have set before the added solution has been well mixed into it it will be necessary again to heat the tubes in boiling water. When thorough admixture has been gained, allow the three jellies to cool. The cooling may be hastened by placing the tubes in ice. When the jellies have set firmly, detach them from the sides of the tubes by plunging them momentarily into hot water. Allow each jelly to fall into a beaker of cold water. Set the vessels aside where they will not be disturbed. Examine the jellies from time to time, and make careful note of the rates at which they swell up.

Can you say from your experiments whether sugar and gum increase the osmotic pressure of the fluid in the jelly?

Note.—You must not think of a jelly as a true solid. For the present think of it as a sponge or network of solid gelatine, containing imprisoned water. When the jelly liquifies it is because the gelatine dissolves, but the system is reversible and the sponge work becomes re-established on cooling.

49. Osmotic pressure demonstrated by diffusion through jellies. Practice

If jellies are, as we have described them, viz., an intimate mixture of solid and liquid, it ought to be possible for substances which are soluble to diffuse through the liquid medium. It is difficult to study diffusion of substances in solutions, because

convection currents are so readily set up and mixing takes place through this cause. Jellies by their rigidity remove such disturbing factors from our experiments, and they are therefore admirably suitable for the study of diffusion.

Carry out the following experiments.

Heat the remainder of the gelatine solution till it liquifies. Measure out 2 cc. of the liquid into each of four tubes and label the tubes.

To No. 1	tube add	0·5 cc. barium chloride solution	(5·0%)
2	,,	0·5 cc. sodium sulphate	,,
3	,,	0·5 cc. copper sulphate	,,
4	,,	0·5 cc. potassium ferrocyanide..	,,

Allow tubes 1 and 3 to cool, and set to jellies. When completely set add to each 4 cc. of gelatine solution, and allow this also to set, so as to form a second layer. Melt the jellies in tubes 2 and 4, and add them respectively to tubes 1 and 3. Allow the third layer in each tube to set.

You have now the conditions arranged for two small experiments on diffusion. In each case the pair of substances will interact, when they meet, and give rise to obvious effects. You will be able, therefore, to note the time taken for the substances to diffuse through a length of gelatine which you can accurately measure.

State how long it takes according to your experiments for a salt to diffuse through one centimetre of jelly.

Note.—It has been found by experiments that the rate of diffusion through jellies is practically the same as through water.

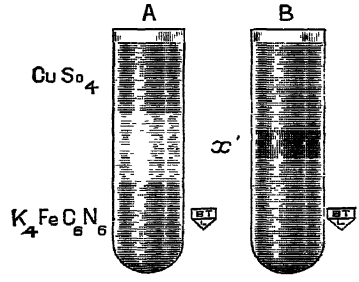


Fig. 13. Diffusion through jellies, illustrating osmotic pressure.

A. Showing the conditions at the start. Copper sulphate and ferrocyanide jellies separated by pure jelly.
B. Condition after about 24 hours. A zone of brown ferrocyanide of copper x^1 formed about the centre of the tube.

50. Osmotic pressure demonstrated by the swelling of gelatine in the presence of acid or alkali. Practice

Measure 5 cc. of 10 per cent. gelatine solution into each of 7 tubes, and add to them as follows :

To	1.	1 drop	H_2SO_4 (50%)
	2.	1 ,,	,, (25%)
	3.	1 ,,	water
	4.	1 ,,	NaOH (6·25%)
	5.	1 ,,	,, (12·5%)
	6.	1 ,,	,, (25·0%)
	7.	1 ,,	,, (50·0%)

These solutions will now all have the same volume.

Allow the solutions to set to jellies. Detach them as before and allow them to fall into cold water.

After 24 hours remove them and determine their volumes by dropping them into a measuring cylinder containing water.

The following results were obtained in a similar experiment :

Volumes of jellies after 48 hours. Temp. 20° C. Original volume in each case = 5·0 cc.

No. 1.	11·5 cc.
2.	8·5 cc.
3.	5·5
4.	4·4
5.	5·0
6.	8·7
7.	10·0

CHAPTER XII

The Physical Properties of Solutions (continued)

51. Surface tension. Theory

The surface of contact between a liquid and a gas or a liquid and a solid is easily shown to be in a special condition of strain. It behaves as though it possessed elastic properties. This phenomenon is exhibited by pure solvents, but the special point of interest here is that the degree of strain at the surface is modified by the presence of a dissolved substance, and this is another proof of the fact that solution is not an inert process, but involves the physical interaction of the solvent and solute.

52. Indirect measurement of surface tension by counting of drops. Practice

Examine carefully a drop of water as it issues from a tap or from a pipette, or similar tube. The pocket lens may help you. If you allow the drop to form at the end of the tube very slowly, you will notice that it develops into a pear-shaped mass, gradually increasing in size until at a certain point it breaks away from the end of the tube and falls. It certainly gives the impression of being held by its upper extremity to the tube as though it were a minute bag being gradually filled with water. It appears as though the outer part of the drop behaved as an elastic membrane. This means that the stronger the surface layer, the larger can the drop become before the weight of the drop is sufficient to detach it from the tube and cause it to fall.

With the same sized end to the tube and the same fluid it is remarkable how constant is the size of the drop. Try this. Draw up distilled water into a small tube (you may use a small graduated pipette or simply a narrow tube marked in some way to indicate a definite volume such as 1 or 2 cc.). See that the water is accurately at the mark indicating some definite volume, and allow the tube slowly to empty itself, under the action of gravitation, noting carefully the number of drops which fall from the tube. You will probably find that for

every cubic centimetre of water you obtain about twenty drops. Repeat the experiment several times. The number of drops which you obtain from 1 cc. of water varies with the shape of the end of the tube, and with such variable conditions as the temperature and purity of the water, but given a constant temperature, using the same water and the same pipette or dropper, you should obtain always the same number of drops from the same volume of fluid.

Repeat the above exercise until you have gained certain control over the pipette. You may also repeat the experiment, using a burette, or you may arrange a rubber tube with a clip either at the upper or the lower end of the dropping tube, by means of which you can regulate the out-flow of the fluid as you desire, and so dispense with the necessity of holding your finger constantly at the upper end.

It is important to realise that the size, and consequently the number of the drops, is independent of the force applied to the liquid to drive it out of the tube. This may be shown by forcing the water out of the tube by means of pressure gently applied to a rubber bag, such as the teat attached to the droppers supplied by the pharmacist. The number of drops per cc. is the same whether the water is forced out of the tube by pressure applied to the rubber bag, or allowed to fall under the influence of gravitation alone.

It is further of importance to realise that the number of drops delivered by the tube from a definite volume of fluid is independent of the time taken for the drops to fall provided the drops are given time enough to form. Try this experiment, taking various times for the emptying of the pipette.

If, in spite of repeated trials, you find a slight difference in the number of drops delivered by the dropping tube, you must understand that this is experimental error, and you must take the mean of your several measurements as being the true value. At the same time you must record carefully the extent of the experimental error. With each experiment or series of experiments you must also record the temperature as the number of drops yielded by the pipette is considerably influenced by this factor.

53. The effect of temperature upon the surface tension of water

Having gained practice in the measurement of the delivery of drops, repeat the experiments described above with both hot and cold water, and record carefully the results obtained at each temperature.

It will probably be clear to the student without further explanation that the greater the number of drops delivered from the same volume the lower is the surface tension. These measurements are of course comparative, and the figures which are obtained do not express the actual force, variations of which are responsible for the variation in the size of the drops, but for practical purposes of measurement the comparative figures are all that we require for the present. Thus, for example, if we find at a certain temperature each cubic centimetre gives twenty-one drops, as compared to twenty at another temperature, we may say that at the second temperature the surface tension is five per cent. higher than at the first, and so on.

54. The surface tension of other pure solvents compared to water

Repeat the above experiments, using the following pure solvents : Ethyl alcohol, paraffin oil, glycerine, and olive oil. Compare the surface tension to that of water in each case.

55. The effect of dissolved substances upon the surface tension of the solvent

Using water as the solvent, determine the effect upon the surface tension of adding the following substances : common salt, soap, ethyl alcohol, acetic acid, glycerine.

In each case express the change due to the addition of the solute as a percentage change in the surface tension.

56. Summary of the experiments so far carried out upon the physical properties of solutions

By the phenomena of diffusion, osmotic pressure, surface tension and lowering of the vapour pressure, we are led to the conclusion that the process of solution of a substance in a liquid is by no means passive and the solvent is certainly not inert. We have seen that it is difficult, if not impossible, to say just where physical changes end and chemical begin, but as a rule where heat is evolved chemical change occurs. In any case it will be wiser for the present not to assume any chemical change unless we can separate a chemically different substance.

CHAPTER XIII

Varieties of Chemical Reactions accompanying Solution

57. Foreword

We have seen that what we called chemical solution is a two-fold process, namely, a chemical reaction followed by the physical process of solution. It is now our business to examine this matter more closely and to consider what kind of chemical changes generally occur when we make use of a chemical solvent.

At present our studies will be confined to solutions made either by adding pure water or water containing some substance, such as an acid, able to effect a change in a solid whereby it becomes soluble in water. In other words, we are concerned with aqueous solutions of various kinds. The reason that we are about to concern ourselves only with aqueous solutions is that our immediate object is the study of the properties of the various metals, and it is by various reactions of their salts that we can best study them. These reactions only occur in the presence of water, for reasons which we shall discuss in later chapters.

It being our object to study the reactions of the metals, and these reactions occurring best in aqueous solutions, it must clearly be our first business to learn how the metals and their compounds can be brought into aqueous solution. And if to bring about solution we need to add anything to the water, we must be in a position to understand what part the dissolved substances play in relation to any other substance added to the solution. For example, we may dissolve metallic zinc in water if we add hydrochloric acid to the water; we have then a solution of zinc chloride, but as we have also a certain amount of hydrochloric acid over and above that which was used up in the interaction with the zinc, the properties of the solution will therefore be those of a mixture of hydrochloric acid, zinc chloride and water, and it is possible that in such a solution some of the properties of zinc will be masked by the presence of the excess of acid.

We shall include most reactions accompanying solution if we consider six types. These types of reactions are considered in Sections 58 to 63. It is to be understood that in verifying each point the student will work in each case with a drop of the solvent and a minute speck of the substance to be dissolved.

58. The substance interacts with water and one of the products dissolves, the other escaping as a gas

Examine the action of water upon sodium amalgam, calcium carbide and sodium peroxide.

When sodium amalgam is added to water, sodium hydroxide is formed and dissolves; hydrogen is formed and escapes.
The mercury may be considered as merely a solvent for the sodium, and does not come into the reaction.

We write the change thus:

$$2Na+2H_2O=2NaOH+H_2.$$

Calcium carbide with water is another similar example.

$$CaC_2+2H_2O=C_2H_2+Ca(OH)_2.$$

The gas C_2H_2, which escapes, is acetylene. The substance which dissolves is calcium hydroxide (slaked lime).

With sodium peroxide and water the reaction is as follows:

$$2Na_2O_2+2H_2O=4NaOH+O_2.$$

59. There is an interaction between the solid and some substance already in solution, with the formation of two substances, one of which dissolves, while the other escapes as a gas

Examine the action of hydrochloric acid or other dilute acid upon calcium carbonate, sulphite, and sulphide, ferrous sulphide, barium peroxide, potassium chlorate, calcium hypochlorite, sodium nitrite. Write equations for what occurs in each case, such as the following:

$$CaCO_3+2HCl = CaCl_2+H_2O+CO_2.$$
$$BaSO_3+2HCl = BaCl_2+SO_2+H_2O.$$
$$FeS+H_2SO_4 = FeSO_4+H_2S.$$
$$2BaO_2+4HNO_3 = 2Ba(NO_3)_2+2H_2O+O_2.$$

60. The products of interaction of solid and solvent dissolve completely in the solvent

Examine the action of water on quick lime or some other hydroxide; dilute acids on slaked lime, and dilute strong acids on various oxides such as mercuric, cuprous, cupric, ferric, cobaltic oxides.

The simplest case is where pure water is both solvent and reagent. We have already noticed such reactions in Chapter VIII.; for example, when water is added to quick lime we have a formation of calcium hydroxide, which then dissolves in the water; the reaction is represented by the equation:

$$CaO+H_2O=Ca(OH)_2.$$

But in the class of reaction considered under this head, solution is generally a result of an interaction between the solid and some substance already dissolved in the solvent, as when slaked lime dissolves in a dilute acid, thus :

$$Ca(OH)_2 + 2H\,Cl = CaCl_2 + 2H_2O.$$

A similar change occurs when other oxides dissolve in acids, for example:

$$HgO + 2H.NO_3 = Hg(NO_3)_2 + H_2O.$$
$$Cu_2O + 2H.Cl = 2CuCl + H_2O.$$

61. The solid forms with the solvent or with some substance already dissolved in the solvent a soluble double compound

(*a*) Examine the case of the precipitation of cupric hydroxide by addition of ammonium hydroxide to cupric sulphate solution and resolution of the precipitate in excess of ammonium hydroxide.

In equivalent amounts cupric sulphate and ammonium hydroxide form cupric hydroxide, but with excess of ammonium hydroxide the soluble double hydroxide, cupric ammonium hydroxide is formed. Thus we write

$$CuSO_4 + 2NH_4OH = Cu(OH)_2 + (NH_4)_2SO_4$$
$$Cu(OH)_2 + NH_4OH = (CuNH_4)(OH)_3.$$

It is owing to this type of reaction that certain salts are able to prevent the formation of precipitates. For example, in the presence of ammonium chloride, magnesium carbonate is not precipitated from solutions of magnesium salts upon the addition of ammonium carbonate solution, by which fact it may be distinguished from calcium or barium. Thus we may write with calcium :

$$CaCl_2 + (NH_4)_2CO_3 = CaCO_3 + 2NH_4Cl,$$

but with magnesium a double salt forms thus :

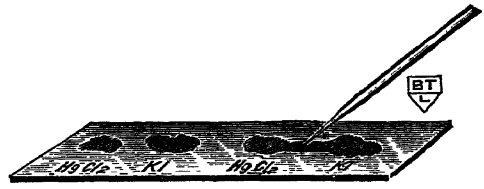
$$MgCl_2 + NH_4Cl = (Mg.NH_4)Cl_3 \text{ (ammonium magnesium chloride).}$$

This double compound is soluble in water, and if it interacts at all with ammonium carbonate we must infer that the corresponding double compound magnesium ammonium carbonate is also soluble in water.

In the light of these examples proceed to study the following cases and write equations to explain what you observe.

In carrying out these reactions do not add quickly one drop to the other, but place the drops side by side upon a glass slide or porcelain plate, then, by means of a fine glass rod, push the one drop towards the other so that they touch without completely mixing. You will then often be able to observe much which would escape your notice if you let the drops mix quickly. (See Fig.) You may, example, see precipitation occur at the point where the drops begin to mix, while further on within the drop of the reagent you may see the precipitate redissolve. In this way you are able to

detect at once whether the precipitate is soluble in excess of the reagent without having to use any more than the one drop of the solution.



(*b*) Examine the following interactions :

(i) Magnesium sulphate and ammonium chloride.
(ii) Magnesium sulphate and ammonium carbonate.
(iii) Magnesium sulphate, ammonium carbonate, and ammonium chloride.
(iv) Zinc sulphate and ammonium carbonate.
(v) Stannic chloride and ammonium sulphide.
(vi) Sodium arsenite and ammonium sulphide.

62. Solution and precipitation constitute a reversible system

A substance is dissolved as the result of combining with some other substance present in the solution, but the compound so formed undergoes decomposition in the excess of water. In other words solution and precipitation depend upon a reversible chemical change in which the variable factor is the concentration of some constituent of the solution.

(*a*) Examine the case of ferrous sulphide and acids.

Take two drops of a dilute solution of ferrous sulphate, and add to one drop a solution of sulphuretted hydrogen. Observe the effect. Now add to the other drop a drop of ammonium hydroxide. Again note the effect. Lastly, by means of a thin glass rod, mix the first two with the second two drops.

If your observations are correct you should have noted the following facts :

The first two drops give no coloration.
,, second ,, a green precipitate or coloration.
,, mixture of all the drops gives a black precipitate or coloration.

The explanation is as follows : Ferrous sulphide is black ; it is readily soluble in very dilute acid, and therefore it cannot be formed by the addition of sulphuretted hydrogen solution to any salt of iron which is formed from a strong acid. If the reaction could occur it would be represented by the equation :

$$FeSO_4 + H_2S = FeS + H_2SO_4.$$

But because H_2SO_4 is a strong acid it is able to decompose the FeS, and therefore the reverse change would also take place, and would be represented by reading the same equation from right to left.

We have already seen in Chapter VIII. that reactions which can occur in one direction or in the opposite direction, according to the conditions, are called reversible reactions. The precipitation of iron sulphide under some conditions and its re-solution under others constitutes a reversible system. The variable condition here is the concentration of the acid present. If the acid is removed as fast as it is formed, by neutralisation by an alkali, there is nothing to hinder the precipitation of iron sulphide, and that is why in the above experiment the black coloration appears when the alkaline drop is added. The object of adding the drop of ammonium hydroxide to a separate drop of iorn sulphate was to show that ammonium hydroxide did not itself form a black compound with ferrous sulphate. You have seen that ferrous hydroxide is green or dirty white in colour. It becomes yellow and brown as it oxidises in the air to ferric hydroxide. The changes which you have observed in this experiment therefore are to be represented as follows :

In the first two drops when mixed.

$FeSO_4 + H_2S = ?$ No obvious change, because FeS is readily dissolved by H_2SO_4.

In the second two drops,

$$FeSO_4 + 2NH_4OH = Fe(OH)_2 + (NH_4)_2SO_4.$$

In the drops all mixed,

$$Fe(OH)_2 + H_2S = FeS + 2H_2O,$$

or you may write equally well,

$$FeSO_4 + H_2S = FeS + H_2SO_4$$
$$H_2SO_4 + 2NH_4OH = (NH_4)_2SO_4 + 2H_2O,$$

and add them together thus :

$$FeSO_4 + H_2S + 2NH_4OH = (NH_4)_2SO_4 + 2H_2O + FeS.$$

The extreme solubility of ferrous sulphide in hydrochloric acid results in it being impossible to precipitate ferrous sulphide from a salt of iron made from such a strong acid, and for this reason you may have a little difficulty in realising that the reaction $FeS + 2HCl$ is truly a reversible reaction. With some other sulphides the reversibility is easily seen.

(*b*) Examine the case of cadmium sulphide and acids.

To one drop of a dilute solution of cadmium sulphate add a drop of a solution of sulphuretted hydrogen. A yellow precipitate forms. Add a drop of a one per cent. solution of hydrochloric acid. The cadmium sulphide rapidly dissolves.

(*c*) Examine the case of copper sulphide and acids.

Repeat experiment (*b*), using copper salts. You will find that copper sulphide does not readily dissolve in a one per cent. solution of hydrochloric acid, but in ten per cent. acid the precipitate rapidly disappears.

63. Solution by the aid of a catalyst

Examine the following cases :

(*a*) A speck of iron or zinc with a minute drop of pure concentrated sulphuric acid.

(*b*) A speck of iron or zinc with a minute drop of 90 per cent. sulphuric acid.

The equation in the second case is generally written : $Fe + H_2SO_4 = FeSO_4 + H_2$.

Since no water appears in the equation you may well ask why in the first case, viz., with strong acid, no reaction, or a very slight reaction, only occurs. It is clear that the water must play a part in the change.

The fact is, however, that with a very small amount of water a large amount of iron and sulphuric acid may be made to interact and the water is still present at the end of the experiment.

We speak of water as exerting **a catalytic action,** and call water acting under these circumstances **a catalyst.** This does not explain at all how it acts. We shall, however, study catalysts in more detail in a later chapter.

CHAPTER XIV

Qualitative Analysis. The Preliminary Examination of a Simple Salt

64. The idea and aim of qualitative analysis

We want to be able to tell rapidly what metal and what acid radicle is present. In the absence of any acid radicle we shall know that we are dealing with an oxide or hydroxide.

In the present and following two chapters we are concerned with simple salts, i.e. such as contain only one base and one acid radicle, but the methods outlined in these chapters can be applied, with only slight modifications, to mixtures of several bases and acid radicles. When several bases are present it becomes sometimes necessary to separate one from the solution before testing for the others, and this involves filtration of precipitates and certain other modifications which necessitate using rather more material than when only one is present, but 50 mg. of material should be ample for any qualitative analysis up to four or five bases and acid radicles.

As regards acid radicles the presence of one does not as a rule interfere with the recognition of another, and no separation is required.

The special points which may arise in the separation of mixtures are considered in Chapter XVII.

65. The plan of work

We divide our work into three parts :

(*a*) Preliminary tests for bases and acid radicles (Chap. XIV.).

(*b*) Systematic and confirmatory tests for bases (Chap. XV.).

(*c*) Systematic and confirmatory tests for acid radicles (Chap. XVI.).

It may happen that with experience the preliminary tests give us all the information we need to enable us to identify the unknown substance. In such a case it may not be necessary to proceed further except with a view to gaining practice in the systematic methods.

But before stating what metal is present we cannot be too sure of our ground, and it is wise, even when the preliminary tests seem conclusive, to run through the systematic tests also.

66. A word about preliminary tests

(*a*) Let your tests be few and well chosen.

(*b*) Carry out your tests always in the same order.

(*c*) Do not be sidetracked into applying confirmatory tests before you have carried out a definite set of preliminary tests.

67. Order of applying preliminary tests

(1) Note the appearance with the naked eye and through the pocket lens. If possible, examine under a microscope.

(2) Observe the action of a drop of water.
Does the drop become acid or alkaline?

(3) Heat a speck of the substance in a dry tube.

(4) If insoluble in water, try solubility in acids.

(*a*) One drop HCl.N
(*b*) ,, HCl conc.
(*c*) ,, HNO_3 N
(*d*) ,, HNO_3 conc.

} These tests may all be carried out on one speck of substance or drop of solution.

(5) Add one drop of H_2SO_4 conc. Warm gently.

(6) Add one drop of NaOH.N and one drop Na_2CO_3.N. Boil.

(7) Add one drop HCl conc. Apply the flame test.

(8) Apply the match test. (See section 20.)

(9) Examine in the borax bead. (See section 21.)

68. Conclusions to be drawn from preliminary tests

1. The appearance.

Colour, form, hardness, specific gravity, streak, efflorescence, deliquescence, signs of oxidation, each may give a clue.

If the substance is colourless many metals are excluded, for example, chromium, manganese, cobalt, nickel, and iron and copper are unlikely. If the substance has a metallic lustre try if it is **magnetic.** A magnet attracts iron, cobalt and nickel. If the substance is black it suggests either carbon, a metal, a sulphide, or the oxide of copper or manganese.

2. Solubility.

All nitrates and nitrites are soluble in water.
All chlorides are soluble in water except of Ag, Pb, Hg(ons).
All sulphates are soluble in water except of Ba, Sr, Ca.
All carbonates, phosphates, silicates and borates are insoluble in water except those of K, Na, NH_4.
The hydroxides and oxides of K, Na, NH_4, Ba, Sr, Ca, Mg are soluble; all others are insoluble.

3. The effect of heat.

(*a*) **Physical changes.**

Melting point.	Low melting point with mineral substance suggest water of crystallisation. Many organic substances have low melting point.
Sublimation.	Without decomposition ammonium salts and many organic substances, arsenic.
Crackling.	Substance which do not readily melt, e.g. $CaSO_4$, NaCl.
Explosion.	Unstable substances, e.g. chlorates, permanganates.
Volatilised.	Without residue. Organic substances of low mol. wt. Some NH_4 compounds.

(*b*) **Chemical changes.**

Sublimation.	With decomposition, NH_4, As, Hg compounds, many organic substances.	
Liquid distillate.	Water, acids, halogens, organic matter.	
Gaseous products.	Colourless	= O_2, CO_2, CO, N_2O, SO_2.
	Dense white	= SO_3, NH_4 salts, conc. mineral acids.
	Coloured	= Violet I_2, brown Br or NO_2, green or yellow Cl_2, black, organic matter decomposed.

4. The action of aqueous acids.

(*a*) Effervescence may be due to

H_2	from metals.	H_2S	from sulphides.
O_2	,, peroxides.	Cl_2	,, hypochlorites.
CO_2	,, carbonates.	Cl_2O	,, chlorates.
SO_2	,, sulphites.	NO_2	,, nitrites

(*b*) Colouration with hydrochloric acid is due to liberation of halogens from oxyhalogen compounds, or NO_2 from nitrites.

(*c*) Precipitation with hydrochloric acid may indicate
(i) Bases such as Ag, Pb, Hg(ons).
(ii) Acids ,, ,, Silicic, boric and many organic acids such as benzoic, salicylic.

(*d*) Colouration with nitric acid may be due to
(*a*) Oxidation, as with ferrous, cuprous, manganous and chromium compounds.

(*b*) Decomposition, as with permanganates, iodides, iodates, bromides, bromates, sulphides, various organic compound.

(*c*) A residue resisting solution suggests silica, tin oxide, silver, lead or mercurous chloride, bromide, or iodide, barium sulphate.

5. Action of concentrated sulphuric acid.

Acid fumes. Chlorides, bromides, nitrates, sulphites, nitrites, oxyhalogen compounds, organic matter.

Coloured fumes. Halogens, nitrites.

Blackening. Organic matter.

Crackling. Unstable compounds, such as chlorates, bromates, iodates, permanganates.

6. Action of sodium hydroxide and carbonate.

Odour of ammonia from ammonium compounds and from organic matter (amines, amides, amino acids).

Precipitate of carbonates of all metals except sodium and potassium, arsenic, antimony.

If there is no precipitate it is certain that **heavy metals are absent.**

Metals present in acid radicles such as ferrocyanides, permanganates or manganates, chromates, etc., would naturally not be precipitated.

7. Flame colourations.

Crimson	= Sr.	Yellow	= Na	Violet	= K.
Red	= Li.	Green	= Ba.	,,	= NH_4
Brick red	= Ca.	Blue green	= Cu.		

8. Match test.

Fe (magnetic), Cu (glistening red), Pb, Ag, Sn (silvery) Notice colours of the flame ; odour of gases evolved

9. Borax bead.

Changes observed in a borax bead

	Oxidising flame		Reducing flame	
	Hot	**Cold**	**Hot**	**Cold**
Copper	Green	Blue-green	Colourless	Brown-red
Iron	Yellow or dark red	Yellow-green	Green	Emerald green
Manganese	Amethyst	Red-violet	Colourless	Colourless
Cobalt	Blue	Blue	Blue	Blue
Nickel	Violet	Red-brown	Grey	Grey

CHAPTER XV

Systematic and Confirmatory Tests for the Base of a Simple Salt

69. How to obtain a solution of a simple compound for systematic tests

If the substance is not yet dissolved, proceed to get it into solution in a methodical way. In the present chapter you are not required to deal with any substance which does not dissolve in simple reagents. The only solvents which you may require are water, hydrochloric acid, or nitric acid. Proceed, therefore, as follows :

(*a*) Take about as much material as would cover the head of a small pin, and add two, three, or even four drops of water. If the substance dissolves either in the cold or on warming, dilute the solution to make twenty drops in all.

(*b*) If after heating with as much as four drops of water the material remains undissolved, add one drop of strong hydrochloric acid. Note any effervescence or colouration if it occurs. If the substance dissolves completely dilute to the desired twenty drops by adding the requisite number of drops of water. If the substance dissolves in part only, add a second or third drop of strong hydrochloric acid. You may also warm the solution. If it dissolves, complete the volume to twenty drops.

(*c*) If it is not dissolved add one, two, or at most three drops of strong nitric acid. Boil the solution till only about three drops remain, and then add drops of water to make the volume as before twenty drops. If only one drop of nitric acid has been used it need not be removed by boiling. But if more is present in the twenty drops, it may interfere with the tests you have to carry out.

Caution. As far as possible you should try to avoid the use of nitric acid, because it is not only an acid, but also an oxidising agent.

70. The division of the bases into groups

(The concentration of the group reagents should be about N/10)

1. To a drop of the solution add a drop of HCl.
 White precipitate indicates **Pb, Ag** or **Hg(ous).**

2. If there is no precipitate add to the previous drop a drop of H_2S water.
 (*a*) Black precipitate indicates **Pb, Hg(ic), Bi,** or **Cu.**
 (*b*) Yellow or brown ,, **Cd, As** or **Sn.**
 Orange ,, ,, **Sb.**

3. If there is no precipitate add to a fresh drop of the original solution a drop of NH_4OH.
 Brown precipitate indicates **Fe.**
 Green ,, ,, **Fe** or **Cr.**
 White ,, ,, **Al.**

4. If there is no precipitate add a drop of $(NH_4)_2S$.
 White precipitate indicates **Zn.**
 Buff precipitate turning brown indicates **Mn.**
 Black precipitate indicates **Co** or **Ni.**

5. If there is no precipitate add a drop of $(NH_4)_2Co_3 + NH_4Cl$.
 A white precipitate indicates **Ba, Sr,** or **Ca.**

6. If there is no precipitate the base must be **Mg, K, Na** or **NH_4.**

Note

(*a*) It is important to understand that the general group reagent may give a precipitate with metals of preceding groups so that these tests must be applied in the order given. For example, the general group reagent for metals of group 2, namely, H_2S, will give precipitates with silver, mercurous and lead salts, so therefore you cannot use the second general group reagent until you have ascertained the absence of members of the first group. But the second group reagent alone will not give a precipitate with any metal of the third, fourth, fifth or sixth groups.

(*b*) In the above series the H_2S is added to the acid solution, i.e. to No. 1, drop, but in every other case the group reagent is added to a fresh drop of the original solution of the salt.

71. Systematic tests for the base of a simple salt

	Group Reagent HCl	Sub-group Reagent NH_4OH
1	Hg· White	Blackens
	Pb White	White Unchanged
	Ag White	White Dissolves
2	H_2S (in acid solution)	$(NH_4)_2S$
	Pb Black Bi Black Cu Black Hg·· Black or yellow Cd Yellow	Insoluble
	As Yellow Sb Orange Sn Brown or yellow	Soluble
3	$NH_4OH + NH_4Cl$	
	Fe·· Dirty green Fe··· Brown	
	Al White Cr Green or violet	
4	$(NH_4)_2S$	
	Co Black Ni Black	
	Mn Flesh colour Zn White	
5	$(NH_4)_2CO_3$	
	Ba White Sr White Ca White	
6	Mg	Na_2HPO_4 White precipitate
	K Na NH_4	No precipitate

72. Confirmatory tests for the base of a simple salt

(To be applied to the original substance or solution.)

Table 3

	Add KI	
1	**Hg**· I Olive **Pb** I_2 Yellow **Ag** I White	
2	**Pb** I_2 Yellow **Bi** I_3 Dark brown **Cu** I Light brown **Hg**··I_2 Red	$BiCl_3$ } are precipitated as oxychloride $SbCl_3$ } when added to excess of water **As** A drop of solution + HCl on copper. Black stain formed on heating. **As** is volatile (see prelim. tests) **Sb** The only orange sulphide (forms oxychloride) **Sn** Reduce with carbon (match test)
3		**Fe** Add HCl + $K_4FeC_6N_6$. Prussian blue
	Fuse original substance with $K_2CO_3 + KNO_3$. Add water $Fe(OH)_3$ brown, $Al(OH)_3$ white, K_2CrO_4 yellow **Fe** **Al** **Cr**	
4	**Ni** Salts are green. **Co** Salts are pink Fuse with $K_2CO_3 + KNO_3$. Add water **Zn** White. **Mn** Green turning to violet	Borax bead (oxidising) **Ni** Violet-brown **Co** Blue **Mn** Amethyst **Zn** White
5	Flame test **Ba** Green. **Sr** Crimson. **Ca** Brick red	$CaSO_4$ Solu. ppts. **Ba** and **Sr** Solutions
6	Flame test **K**, $\mathbf{NH_4}$ Violet. **Na** Yellow	**K** Flame best seen through blue glass $\mathbf{NH_4}$ Yields NH_3 when heated with NaOH

73. The division of groups into sub-group

The colour of the precipitate in a group may distinguish the metal from all others, but where several metals in one group give the same colour we add a sub-group reagent to distinguish them.

With a simple salt we shall only have real need of a subgroup reagent when we have to distinguish the sulphides of group 2, but in separation of several bases the subgroup reagents become of importance.

Since subgroup reagents are used largely for their solvent action they should be more concentrated than the group reagents. The concentration called " normal," or twice " normal," is suitable.

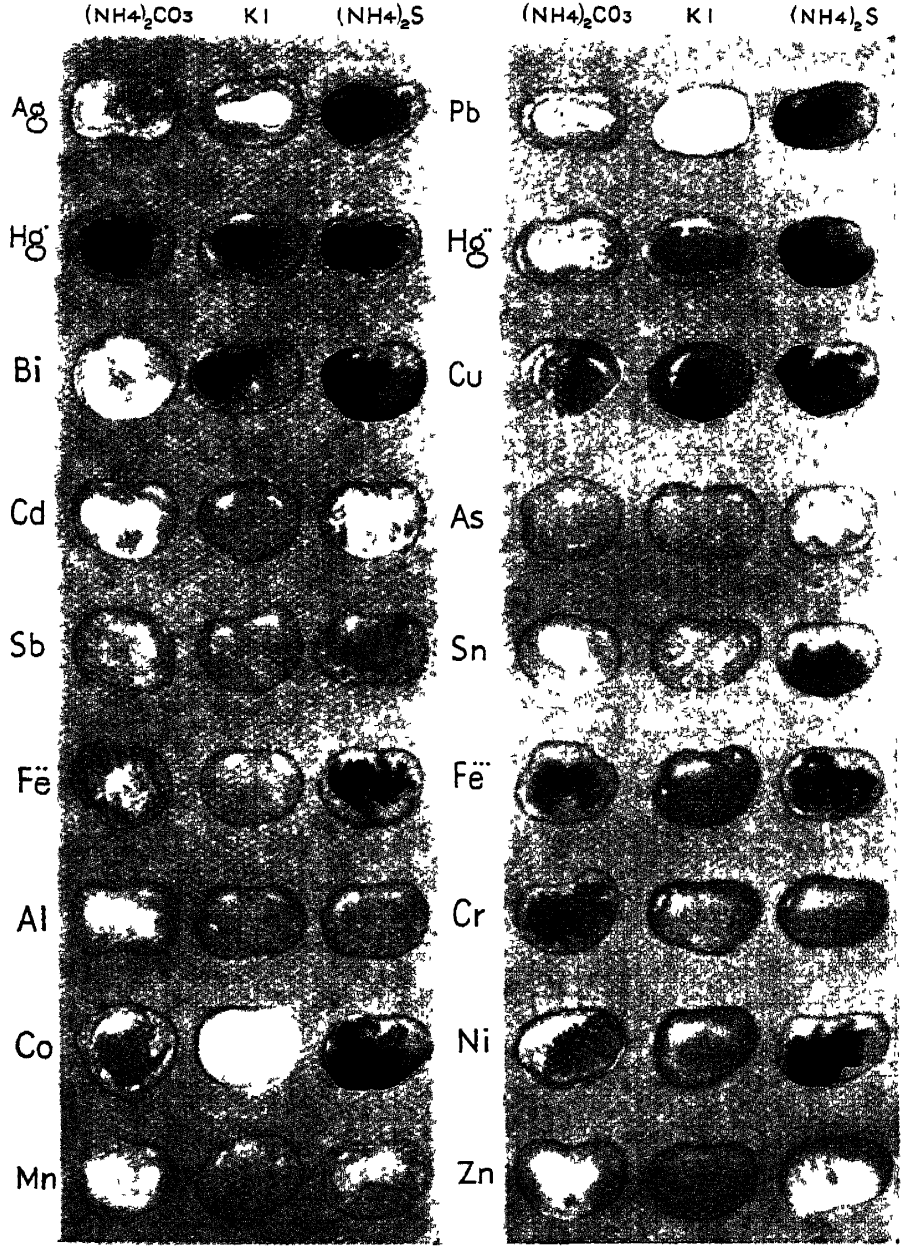
Note. About the concentration of reagents

Although the tests in this chapter are styled qualitative it must be thoroughly understood that in all chemical reactions the concentration of the reagents is a most important factor. You should never use any reagent without knowing its concentration.

Reagents used for precipitation may conveniently be made decinormal.

Reagents used as solvents such as HCl, NH_4OH $(NH_4)_2S$ may be made normal.

THE RECOGNITION OF THE COMMON METALS
✣ USING THREE DROPS OF THE SOLUTION ✣



74.

In the following table several confirmatory tests are combined. By means of it the presence of any metal may be verified at a glance, since no two metals give the same reactions.

Table for the detection of any single common metal, using three drops of the solution.

(See also the coloured plate, facing page 65.)

	Ammon. Carbonate	Ammon. Sulphide	Potassium Iodide
Silver	White	Black	White
Lead	White	Black	Bright yellow
Mercurous	Black	Black	Olive
Mercuric	White	Black	Red
Bismuth	White	Black	Dark brown*
Copper	Blue	Brown	Light brown
Cadmium	White	Yellow	—
Arsenic	—	*Yellow	—
Tin	White	*Yellow	—
Antimony	White	*Orange	—
Ferrous	Dirty white	Black	—
Ferric	Brown	Black	—
Aluminium	White	White	—
Chromium	Green	Green	—
Zinc	White	*White	—
Manganous	White	Yellow turning buff	—
Manganic	Brown	Brown	—
Nickel	Green	Black	—
Cobalt	Amethyst	Black	—
† Barium	White	—	—
† Strontium	White	—	—
† Calcium	White	—	—
† Magnesium	White	—	—
† Sodium	—	—	—
† Potassium	—	—	—

The colour refers to the precipitate.
The sign * means that the precipitate is soluble in excess of the reagent
† The group in brackets must be distinguished by the flame test.

75. Some special confirmatory tests

Copper

The blue colour of alkaline solutions

When ammonium sulphide is added to the solution of a copper salt a blue zone appears beyond the margin of the mixing drops. The ammonium sulphide solution used contains excess of ammonium hydroxide, and when the sulphide is precipitated at the junction of the two drops the ammonium hydroxide diffuses past the precipitate and forms copper hydroxide, which is pale blue, and this in turn dissolves in excess of ammonium hydroxide to form the dark blue cupric ammonium hydroxide. This reaction is very characteristic of copper. (See coloured plate, facing p. 65.)

Arsenic

Reduction to the metal

Most tests for arsenic depend upon separating the element by reduction. To distinguish arsenic and tin place a drop of the solution with a drop of hydrochloric acid (N) on a strip of clean copper foil and gently heat the drop. A black deposit indicates arsenic. The black deposit is metallic arsenic, which is formed because copper has a greater affinity for oxygen or other negative radicles than has arsenic. Copper acts as a reducing agent. Thus :

$$As_2O_3 + 3Cu + 6HCl = 3CuCl_2 + 2As + 3H_2O.$$

Another good test is heating a minute quantity of the substance with potassium cyanide and carbonate in a fusion tube. The arsenic sublimes. If examined with a pocket lens it will be seen to be crystalline (distinction from mercury). The essential reaction is an oxidation of the cyanide to cyanate at the expense of the oxygen of the arsenic compound thus :

$$As_2O_3 + 3KCN = 2As + 3KCNO.$$

Another important test for arsenic which likewise depends upon a reduction is called the Marsh test. In this case the reduction is effected by nascent hydrogen. Zinc and dilute sulphuric or hydrochloric acid are allowed to interact, and the substance suspected to contain arsenic is added while the hydrogen is being produced. Arsenic hydride is formed, and is carried up with the escaping hydrogen. By means of a long tube the arsenic may be collected. To do this the tube must be heated in the flame at the near end. Arsenic will be found deposited beyond the point of

heating. The arsenic may likewise be detected in the hydrogen gas by allowing the gas to impinge when alight upon a cold white plate, or the gas may be brought into contact with a piece of filter paper on which is a spot of silver nitrate solution. Metallic silver is formed.

$$6AgNO_3 + AsH_3 + 3H_2O = H_3AsO_3 + 6HNO_3 + 6Ag.$$

In applying the test in this way it is essential that no H_2S should be present in the hydrogen, else a black precipitate of silver sulphide might be mistaken for metallic silver.

Antimony, bismuth

Oxychloride formation

This fact must not lead to confusion with the first group metals. On heating with HCl conc. the oxychloride is converted into the chloride and the solution becomes clear.

$$BiOCl + 2HCl = BiCl_3 + H_2O.$$
$$SbOCl + 2HCl = SbCl_3 + H_2O.$$

On adding the chloride solution to a large volume of water the oxychloride is reprecipitated. Thus the reaction is reversible.

$$SbCl_3 + H_2O \rightleftharpoons SbOCl + 2HCl.$$
$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl.$$

Iron, aluminium, chromium

Distinction by sodium peroxide

If a speck of sodium peroxide is added to a drop of the solution in question, chromium compounds yield the higher oxide or peroxide of chromium, called often chromic acid, and this forms with the sodium hydroxide sodium chromate, which is yellow and soluble. Ferric salts undergo no such change, but yield a precipitate of brown ferric hydroxide, whereas ferrous salts become oxidised to ferric and then yield the brown ferric hydroxide. Aluminium salts yield a white precipitate of aluminium hydroxide, soluble in excess.

Ferric salts are distinguished from ferrous not only by the colours with ammonium hydroxide (ferric brown and ferrous green) but also by potassium ferricyanide (ferric brown, ferrous blue), or by potassium sulphocyanide (ferric, blood red, ferrous, no change).

But remember ferrous salts rapidly oxidise to ferric.

Nickel, cobalt

Possible confusion with iron

If when iron is present ammonium sulphide were added, FeS, which is black, would be formed. As a caution, therefore, test the black precipitate by adding N.HCl in the cold. FeS dissolves, CoS and NiS are insoluble.

Potassium

Potassium salts differ from sodium salts in giving certain precipitates. Sodium tartrate added to a potassium salt, in concentrated solution, gives a white precipitate (cream of tartar).

Platinum chloride is also sometimes used as a reagent. It gives a golden precipitate with potassium and also with ammonium salts.

CHAPTER XVI

Confirmatory and Systematic Tests for Acid Radicles

The preliminary tests (Chapter XIV.) may have suggested what acid radicle is present ; if so, it remains only to apply confirmatory tests, but if the preliminary fail to suggest the acid to us we must follow out a methodical plan to find out what it is. The confirmatory tests are given in Section 76 and the systematic plan in Section 77.

76. Confirmatory tests for acid radicles

Nitrous and nitric acids

In the presence of a reducing agent, from the former dilute, and from the latter concentrated acids liberate nitric oxide which reacts with ferrous sulphate to form a complex dark brown coloured substance. To carry out the test mix a drop of the solution with a drop of ferrous sulphate on a glass slide or tile, bring near the mixed drops a drop of dilute sulphuric acid. A brown ring where the drops meet indicates a nitrite. Nitrates only give this reaction if concentrated sulphuric acid is used.

Even with exceedingly dilute acid solutions, nitrites give blue colouration to potassium iodide and starch.

Sulphuric, sulphurous and hyposulphurous acids

Sulphuric acid gives with $BaCl_2$ a white precipitate of $BaSO_4$ insoluble in dilute acids. The other two acids are reducing agents, and confirmatory tests should easily suggest themselves. A drop of iodine solution will be decolourised, or a drop of potassium permanganate or bichromate or of ferric chloride. It follows also that these acids are in turn tests for permanganates and chromates.

After oxidation by HNO_3, Br or I, the SO_4 radicle can be detected by the addition of $BaCl_2$.

The halogen acids, hydrocyanic, ferrocyanic and sulphocyanic acids

Hydrofluoric acid etches glass. Chlorides, bromides, iodides and cyanides give precipitates with a silver solution. The first three are confirmed by adding a drop of H_2SO_4 conc. and a speck of MnO_2. (The free halogens are liberated.) Cyanides are distinguished by adding a trace of ferrous sulphate and sodium hydroxide and warming; this forms sodium ferrocyanide. A drop of ferric chloride now gives the characteristic prussian blue colour which was obtained in the test for iron.

Sulphocyanides give with ferric chloride a blood red color.

Oxyhalogen acids

The hypohalites yield halogens when treated with dilute weak acids. They yield oxygen when treated with hydrogen peroxide.

Halates are more stable in solution than hypohalites, but with mineral acids the halogens are liberated.

Concentrated mineral acids liberate from chlorates a mixture of chlorine and the oxide of chlorine.

Boric and silicic acids

They are solid acids exceedingly feeble in combining power, and therefore readily liberated from salts by weak acids. Their insolubility distinguishes them readily from other acids, and they are distinguished from one another by the fact that while silicic acid is quite insoluble, boric acid will dissolve on heating with sufficient water, and it recrystallises in platelets on cooling. Under the microscope the difference is very obvious.

Carbonic acid

Precipitates lime water, the precipitate being completely soluble in acids. Carbonic acid is liberated rapidly by very weak acids even in the cold.

Phosphoric acid

A phosphate gives a white crystalline precipitate of magnesium ammonium phosphate when treated with magnesium sulphate to which ammonium chloride and ammonia have been added.

If warmed with ammonium molybdate in the presence of nitric acid, a phosphate gives a yellow precipitate of ammonio phospho-molybdate easily soluble in ammonia.

Arsenious and arsenic acids

Arsenites reduce, and hence discharge the colour of iodine solutions.

Boiled with ammonium molybdate and nitric acid arsenites and arsenates give a yellow precipitate of ammonium arseno molybdate. The precipitate is soluble in ammonium hydroxide and cannot be distinguished by appearance from ammonium phospho molybdate. All arsenic compounds are readily reduced to the metal (see arsenic confirmatory tests).

Table for the identification of some organic acids

		The effect of heat*	A crystal or drop of solution +1 drop $K_2Cr_2O_7$,N +1 ,, H_2SO_4conc.	A drop of solution +1 drop acetic acid. N +1 ,, $CaCl_2$.N.
Liquid and volatile	Formic	Acid vapour	Gas evolved No colour change	No precipitate
	Acetic	Odour of vinegar Acid vapour	No gas No colour change	Ditto
Solid, crystalline non-volatile	Oxalic	Gas evolved Does not char	Gas evolved No colour change	White precipitate
	Succinic	No gas Does not char	No gas No colour change	No precipitate
	Tartaric	Chars rapidly	Gas. Solution turns green	Ditto
	Citric	Chars slowly	Ditto	Ditto.

* When the acid is combined with a base, add 1 drop H_2SO_4 and then heat gently.

Chromic, manganic and permanganic acid

A drop of the solution + drop of H_2SO_4 conc. + drop Na_2SO_3 or $Na_2S_2O_3$.
Chromic acid yield green chromium sulphate.
Manganic „ „ colourless manganese sulphate.
Permanganic „ colourless manganese sulphate after passing through the green colour of the manganate.
Salts of these acids are distinguished by their colours, and after reduction, as above, the bases Fe and Mn can be precipitated by NH_4OH, $(NH_4)_2S$, etc.

77. Systematic tests for the acid radicle

If the preliminary tests have been followed with care about the only acid radicles which could have escaped detection are those of sulphuric and phosphoric acid. Therefore, proceed at once to apply the confirmatory tests for these two acids (see Secti n 76). If neither acid can be detected it must be that thro gh some oversight in the preliminary tests the acid has been missed. The following systematic plan may therefore be adopted, which is also useful where more than one acid radicle is present.

Before examining systematically for the acid radicle, it is necessary to know how it is combined.

There are three possible cases :—

(1) No heavy metals are present.

(2) Heavy metals are present, but the salt is soluble in water or dilute acid.

(3) The salt is insoluble in water or acids.

In case (1) proceed direct to Table A.

In case (2) add sufficient sodium carbonate to precipitate the heavy metals, and boil, filter away the carbonates of heavy metals and acidify with nitric or acetic acid (having previously shown one of these acids absent by tests, Section 76). Proceed as in Table A.

In case (3) If organic follow the table in Section 76.
If inorganic fuse the substance with sodium and potassium carbonate, add water, boil, and proceed as in case (2).

Table A

Systematic tests for acid radicles

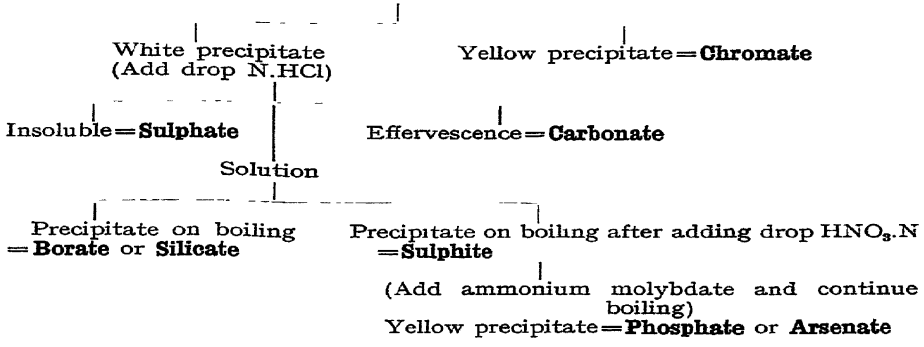
(*a*) If organic follow the table in Section 76.

(*b*) If inorganic test for **Nitrate** or **Nitrite** (see Section 76).

(*c*) To a drop of the solution add a drop of HNO_3.N + a drop $AgNO_3$.N/10.

A precipitate may be **Chloride, Bromide, Iodide, Cyanide** (see Section 76).

(*d*) To another drop of the original solution add a drop of $BaCl_2$.N/10.



CHAPTER XVII

The Separation of Mixtures

78. The amount of material and the concentration of the solution to use

Consider at each step how much reagent you require before you add it; in this way you will always know at any rate the order of concentration with which you are dealing, and you will obviate diluting your solutions to a degree which makes work difficult and wasteful.

For qualitative analysis use about 10 mg. of material for every base present, dissolved in about 20 drops of water. This gives a

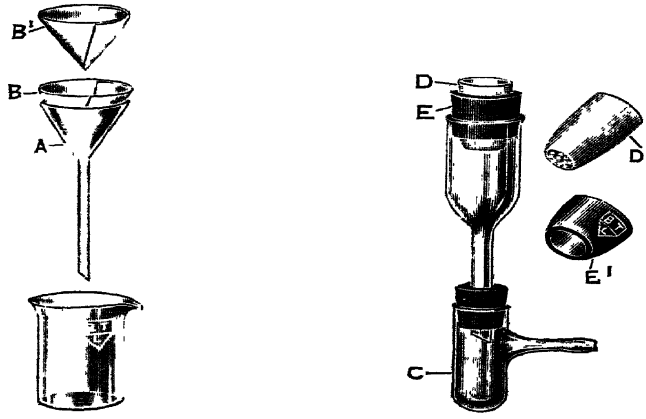


Fig. 14. Filtering Apparatus.

A. Filtering funnel about 5 cc. capacity.
BB¹. Filter paper folded.
DD¹. Filtering crucible (perforated bottom).
EE¹. Rubber ring to support the crucible in funnel.
C. Stout glass collecting tube connected by side tube to water suction pump.

concentration of a salt of the order of decinormal N/10 (see volumetric analysis, Chapter XVIII. If, for example, the salt were silver nitrate it is clear that 2 drops of HCl.N would be amply sufficient to precipitate the whole of the silver as chloride.

It will be seen that a decinormal solution of a salt is of the order of 1 per cent. If the solution is much more concentrated precipitates will carry down impurities with them by absorption, and these impurities may lead to erroneous conclusions as to the nature of the precipitate. On the other hand, excessive dilution is wasteful. Try to keep between the limits of decinormal and centinormal.

Analysis of mixtures differs mainly from analysis of simple salts in that the group precipitates must be filtered off and separately tested.

79. The plan of separation of several bases when phosphates are absent

To a drop of the solution add a drop of HCl.N and a drop of H_2S. If there is no precipitate use Table B, omitting the use of H_2S. If there is a precipitate follow the whole table in every detail.

Table B

Add HCl filter if necessary

- filtrate — pass H_2S through warm solution
- precipitate = group (1) — $AgCl$, $PbCl_2$ $HgCl$
 - precipitate = group (2)
 - (*a*) PbS, HgS, CuS, Bi_2S_3, CdS
 - (*b*) As_2S_3, Sb_2S_3, SnS or SnS_2

(1) Evaporate the solution to dryness, heat to char organic matter, add HCl one drop + HNO_3 one drop, evaporate again to dryness, add again HCl one or two drops to dissolve the residue, dilute with water to 2 or 4 c.cs. (see Section 80).

(2) Add five drops NH_4Cl and as many drops of NH_4OH as are necessary to make the solution alkaline and completely precipitate any metals of the third group which may be present

- filtrate — (add $(NH_4)_2S$)
- precipitate = group (3) — $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$
 - filtrate — (add $(NH_4)_2CO_3$)
 - precipitate = group (4) — CoS, NiS, MnS, ZnS
 - filtrate — (add Na_2HPO_4)
 - precipitate = group (5) — $BaCO_3$, $SrCO_3$, $CaCO_3$
 - filtrate — Evaporate. Heat to expel NH_3. Test for Na and K.
 - precipitate = $Mg.NH_4$, PO_4

80. Modifications necessary when phosphates are present

When the phosphoric acid radicle is present it must be removed, because otherwise, upon the addition of ammonium hydroxide, the phosphates of many bases would be precipitated.

It is usual to remove the phosphoric acid immediately before passing to the third group. To do this proceed as follows :—

Add excess of a saturated solution of sodium acetate and filter. The precipitate contains **Fe**, **Al** or **Cr** as phosphates.

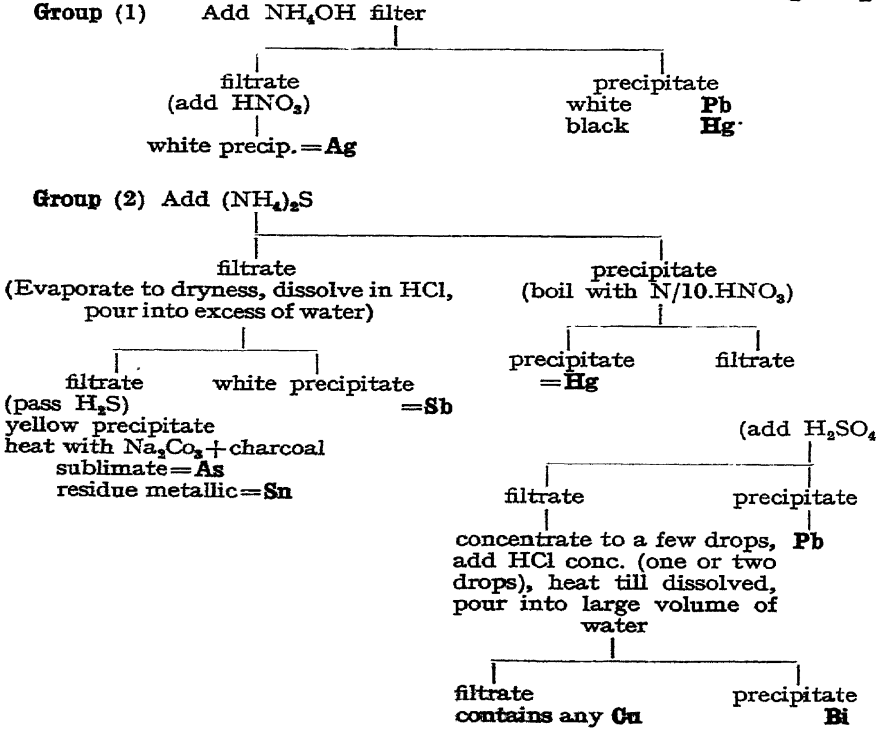
Remove a drop of the filtrate and test if iron is present, then add to the remainder of the solution ferric chloride drop by drop till no further precipitate occurs. Boil the solution, if necessary adding more ferric chloride, so that the solution as well as the precipitate is coloured.

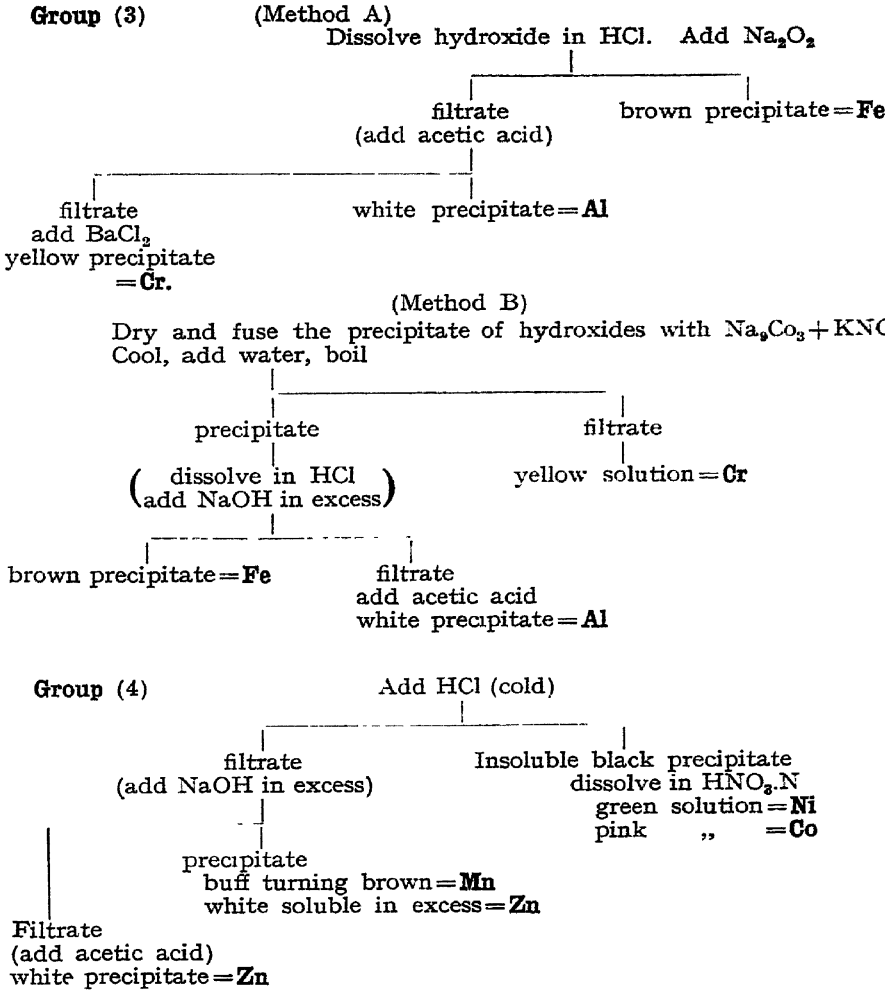
The precipitate consists of ferric phosphate, and it can be rejected.

The solution contains excess of iron.

The phosphate, having been removed, you may now proceed exactly as in Section 79.

81. The separation of the bases within each group





82. The identification of several acid radicles

The preliminary tests and the systematic tests described in Section 77, Chapter XVI., generally suffice, even if several acid radicles are present, for the presence of one does not usually affect tests for another. An exception might be where chlorides, bromides and iodides were mixed, or phosphates and arsenates. In such cases are good exercises for the student in applying the principles he has learned.

CHAPTER XVIII

Volumetric Analysis

83. The idea of volumetric analysis

In volumetric analysis we compare volumes instead of weights. Suppose we want to know how much sodium carbonate there is in a sample of water. It would be tedious to evaporate the solution to dryness and carry out a gravimetric analysis. All we need to do is to add an acid solution of known concentration gradually until all the alkali has been neutralised. We can calculate from the volume of acid solution employed how much alkali is present. Conversely if we had an acid solution, by using a solution of an alkali of known concentration we could determine the concentration of the acid. The method requires that we should have to start with one solution of known concentration; from it we can, by comparison, determine the concentration of many other substances in solutions, or the weight of various solid substances which neutralise or react with the standard solution.

Standard solutions (Normal solutions)

We could use any solution of definite concentration as our standard provided it interacted with the substance we wish to analyse, but it is much more convenient to fix upon some definite universal standard for solutions, so that in any laboratory we may know that the solutions correspond to one another, and contain some fixed quantity of substance. This obviates our continually asking what the concentration of the solution may be, and it avoids mistakes.

It would be better always to use ten per cent. solutions than to be changing our standards continually. But there is yet a better and simpler way, namely, to use solutions which are exactly equivalent to one another, i.e. so made that one drop of the one will neutralise one drop of the other.

We therefore take as our standard in volumetric analysis a solution which contains in each litre an amount of substance equivalent to one gram of hydrogen. In the case of acids used to

neutralise alkalies in volumetric analysis we take a weight of acid equivalent to the molecular weight divided by the number of hydrogen atoms in the molecule, which are displaceable by bases. Thus in sulphuric acid we have two hydrogen atoms which are displaced by bases, and we need therefore to take for a standard solution a molecular weight in grams, viz., 98 grams divided by 2, to make a litre of solution. It is very important for the student to realise that the hydrogen atoms must be truly displaceable, if they are to be considered in calculating the amount of substance to be used for a litre of solution. For example, there are two closely allied acids, carbonic acid H_2CO_3 and formic acid H_2CO_2; both contain two hydrogen atoms per molecule, but in the first two and in the second case only one is displaceable by bases. We say carbonic acid is dibasic, but formic acid is monobasic. Thus we write:

$$H_2CO_3 + 2NaOH = Na_2CO_3 + 2H_2O$$
$$H.CO_2H + NaOH = Na.CO_2H + H_2O.$$

The difference is best understood from the structural formulae which are as follows:

Carbonic acid HO—CO—OH
Formic acid HO—CH=O.

We observe that in the first case each hydrogen is attached directly to an oxygen atom, and in such case it is displaceable by bases, but in the second case one of the hydrogens is attached to the carbon, and in this case it is not displaced by bases.

Therefore to make standard solutions of carbonic acid we should take half, and of formic the whole, of a molecular weight in grams for each litre of solution. Such solutions would then both have the same neutralising power, and would also be equivalent to the hydrochloric acid we have previously considered.

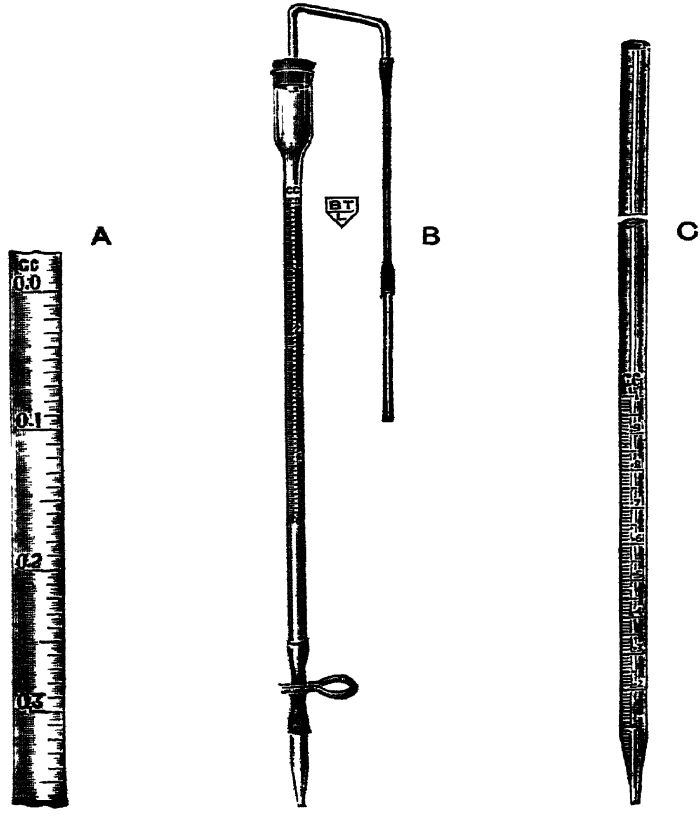
To make a standard solution of an alkali we shall clearly require to take for each litre a weight in grams divided by the number of displaceable atoms of metal in the molecule. Thus of sodium hydroxide we require a molecular weight, of sodium carbonate half a molecular weight, and of calcium hydroxide likewise half a molecular weight, as the following equations show:

$$NaOH + HCl = NaCl + H_2O.$$
$$Na_2CO_3 + 2H.Cl = 2Na.Cl + H_2O + CO_2.$$
$$Ca(OH)_2 + 2H.Cl = CaCl_2 + 2H_2O.$$

84. The practice of acidimetry and alkalimetry

(Titration of acids by alkalies and vice versa)

There are several ways of ascertaining that the solution is neutral, but the simplest is by means of an indicator, i.e. some substance which in an acid solution has one colour and in an alkaline solution another. The colouring matters of many plants might be used, but they often fade rapidly; litmus, however, derived from a plant is used considerably as an indicator. Generally we prefer such artificial compounds as phenolphthalein or methyl orange, which are very stable. If a minute amount



of phenolphthalein is added to an acid solution no colour is observable, but if alkali is added until the solution is neutralised any further addition of alkali gives an immediate red colour. We know, therefore, by this means that we have added enough

alkali to neutralise the acid present, and if we know the concentration of the alkali we can calculate the concentration of the acid or the amount of acid present.

(*a*) Given a standard solution of sodium hydroxide (normal or decinormal), ascertain the amount of hydrochloric or other mineral acid present in a solution, using phenolphthalein as indicator. The appearance of the slightest pink colour indicates the complete neutralisation of the acid. The reaction is:

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O.$$

Repeat the above titration until you get concordant results.

You should aim at an accuracy of 1 per cent.; therefore, if your burette is graduated with one hundred divisions per cc., 1 cc. may suffice for titrations, but if there are only fifty graduations per cc. you will need to take 2 cc. at least, and so on.

(*b*) Breathe through a tube allowing the expired air to bubble through the pink solution, notice the disappearance of the pink colour. Explain the change.

(*c*) Measure into a small flask or test-tube a definite amount, say, 1·0 cc. of NaOH.N/10, add a drop of phenolphthalein solution and breathe as before through a tube into the alkaline solution until the pink colour disappears. Note the time required to decolourise the solution.

From experiment (*c*) calculate the amount of carbon dioxide produced from your body in 24 hours,* assuming the rate of production of the gas to be constant.

In making this calculation it must be understood that the following reaction takes place when CO_2 is bubbled through sodium hydroxide solution:

$$NaOH + CO_2 = NaHCO_3,$$

or, since we know water plays a part, we may write:

$$2NaOH + 2H_2CO_3 = 2NaHCO_3 + 2H_2O;$$

neutralisation is reached when we have converted all the alkali into sodium bicarbonate. A trace of carbonic acid in excess of that required to transform all the hydroxide into bicarbonate is now free to act upon the red indicator and turn it white.

(*d*) Repeat experiment (*a*) and (*b*), using methyl orange as an indicator. You will find that the yellow colour is not changed to red, however long you bubble CO_2 through the solution, although if you titrate the alkali with a mineral acid such as HCl you will get the same result as if you used phenolphthalein. Methyl orange, therefore, is not sensitive

to CO_2, and an end point is reached only when a mineral acid is present in excess. The slightest excess is sufficient to turn the methyl orange to red.

It is evident that it is not a mere question of the amount of acid which determines the change of indicator colours, but also the kind of acid.

We have learned that indicators vary in sensitivity and cannot all be employed for the same purpose, also that acids vary in their behaviour towards indicators, some being able and others unable to alter the colours of indicators. Such acids as are able to change the colours of all indicators we call **strong acids,** while those unable to do this we call **weak acids.**

We can best explain these peculiarities of acids by means of the ionic theory. It is, however, well that the student should first become familiar with the facts. We may summarise the facts we have observed so far by saying that acids fall into two classes.

(i) Acids which when present even in minute concentration are able to alter the colour of indicators.

When we titrate alkalies with such acids we find that the moment a drop of acid is added over and above that required to neutralise the alkali, a sudden sharp change of colour in the indicator is observable. These acids are such as have in many other respect great activity, and we call them strong acids; they are generally mineral acids. Examples are HCl, HBr, HNO_3, H_2SO_4.

(ii) Acids which only affect some indicators, as, for example, carbonic acid, which acts on phenolphthalein and litmus, but does not act upon methyl orange.

Such acids require to be titrated with specially selected indicators and the end point is often not sharp, but appears gradually. It follows that such acids are sometimes difficult to titrate. These acids are such as we have learned to consider as weak acids, for they are readily displaced by strong acids from their salts. Such weak acids have none of the violent properties which belong to strong acids. Examples of weak acids are carbonic, hydrocyanic, silicic, phosphoric, and most organic acids.

85. The choice of indicators

The theory of indicators likewise demands a knowledge of the ionic theory, but even without a knowledge of this theory we may profitably make use of indicators and carry out many useful operations, provided we remember certain rules. These rules apply to the kind of acid or alkali and indicator which must be selected for a titration. They are as follows:

Rules for titration

Base	Acid required	Indicator required
Strong base	Strong acid	Any indicator
	Weak acid	Special indicator
Weak base	Strong acid	Special indicator

In a word: at least one of the reagents must be strong, and unless both are strong a special indicator must be employed.

As regards the nature of the special indicator, all we need say at this stage is that when a weak acid is being titrated we must employ an indicator of such a nature that it will be decomposed by the acid ; otherwise we could not ascertain the precise point at which the weak acid was in excess. In other words the indicator selected is a compound of an acid much weaker than the acid we are titrating. Phenolphthalein, for example, is a colourless substance of reebly acidic properties which forms salts which are coloured red. Such salts are decomposed by any acid stronger than the indicator and the colourless compound formed. When we are titrating by means of a strong acid we can employ an indicator which is more acidic in properties than phenolphthalein. For example, methyl orange is a mixture of a red acidic substance and its yellow sodium salt Any strong acid changes the yellow to the red substance, that is to say, liberates the red acid from the yellow salt.

Advantage may be taken of the difference in acidic properties of indicators in titrating mixtures of an alkali and an alkaline salt.

As an example, we may consider the estimation of a mixture of sodium hydroxide and sodium carbonate by means of a standard solution of sulphuric acid.

86. The estimation of a mixture of hydroxide and carbonate

(A) Measure out a definite volume of the alkaline solution and add a drop of phenolphthalein solution ; carefully run in the acid, stirring or gently shaking the solution the whole time until the pink colour vanishes. At this point the whole of the sodium carbonate has been changed to bicarbonate, as in the equation

(i) $Na_2CO_3 + HCl = NaHCO_3 + NaCl$.

The total HCl needed, therefore, just to decolourise the phenolphthalein is the amount required to completely neutralise the NaOH and to half neutralise the Na_2CO_3.

We can ascertain what this half amounts to by continuing the titration with methyl orange as indicator, for with this indicator the end point is reached only when the Na_2CO_3 has been turned completely into NaCl as in the equation.

(ii) $Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2$.

(B) Now add a drop of methyl orange and continue the titration till the colour is red. The other half of the carbonate is now neutralised. The difference, therefore, between the first and second readings of the burette represents half the carbonate present in the volume titrated.

With N/10 acid, 1 cc. difference = ·0044 grms. CO_2.

Note.—1 cc. N/10 carbonic acid = ·0022 grms. CO_2, but in the above method we are titrating by difference bicarbonic acid $H.HCO_3$, in which case 1 cc. N/10 bicarbonic acid is equivalent to ·0044 grms. CO_2.

87. Some practical applications of acidimetry and alkalimetry

(*a*) In the given sample of sodium carbonate (mixture of hydrous and anhydrous) determine the percentage of water by titration.

(*b*) Household baking powder may be sodium bicarbonate, or a mixture of this substance with flour or other neutral substances. Determine by titration the percentage of sodium bicarbonate in the sample supplied to you.

(*c*) Household soap is the sodium salt of one or more fatty acids. Fatty acids are complex weak organic acids. Pure soaps should be practically neutral, but common soaps often contain free alkali (sodium hydroxide) and some soaps are adulterated with sodium carbonate. In the sample of soap or soap solution supplied to you determine the percentage of free alkali.

Is the alkali present as hydroxide or as carbonate?

How could you estimate the amount of sodium in combination with the fatty acid of the soap?

(*d*) The molecular weight of a fatty acid, if it were monobasic, would be the proportion between the weight of fatty acid and one gram molecular weight of sodium hydroxide which enter into combinations, or the weight of fatty acid which neutralise 1 litre of normal sodium hydroxide.

Determine the molecular weight of the fatty acid in the sample of sodium oleate (castile soap) given to you.

(*e*) Determine the mean molecular weight of the mixture of fatty acids present in candle grease (stearine). Fatty acids of high molecular weight do not dissolve in water, but they dissolve in alcohol, and in this solution may be titrated with alkali, using phenolphthalein as indicator. The alcohol must be mixed with a little water 10–20 per cent. (methylated spirits suffices for the experiment).

(*f*) Fatty acids have the general formula $C_nH_{2n+1}COOH$; it is the last H which reacts in titration thus :

$$C_{15}H_{31}COOH + NaOH = HOH + C_{15}H_{31}COO.Na.$$

Write the formula for the fatty acid present in castile soap as far as you can judge from your results in Ex. 4.

(*g*) The acid properties of natural vinegar are due to acetic acid, which has the formula CH_3COOH. It should be clear from the formula that the acid is monobasic.

In the sample of vinegar, determine the percentage of acetic acid.

Is any mineral acid present in the sample? What is the nature of the mineral acid? What is the percentage of mineral acid present?

Do you consider this amount of mineral acid would be harmful?

(*h*) Acidity in wine, milk, bread, and many other foods results from the growth of fungi or bacteria; such acidity is therefore indicative of impurity, and the percentage of acid present is some guide as to the extent of decomposition which has taken place.

Estimate the acidity of milk from time to time during the day, or during several days. Plot a curve, showing the rate of decomposition of the milk as judged by the production of acid. The acid is lactic acid, a weak organic acid of formula $CH_3CH.OH.COOH$. It is a monobasic acid.

Calculate the percentage of lactic acid in the milk from time to time. Repeat the above experiment on milk after adding a few drops of an antiseptic such as formalin to the milk.

Carry out similar experiments with bread. The acids may be washed out with hot water, or the titration may be carried out with the bread suspended in warm water.

(*i*) Calcium carbonate or hydroxide are the only substances present which can neutralise acids. Determine the percentage of either or both if present in the samples supplied (mortar, cement, impure chalk, limestone, marble).

(*j*) The temporary hardness of water is due to dissolved calcium bicarbonate. It is called hardness because it causes difficulty in action of soap in water. Soap will not cause a frothing (lather) in hard water because a calcium soap is precipitated by interaction of the sodium soap with calcium bicarbonate. The temporary hardness may be removed by boiling the water which causes a loss of CO_2 and a precipitation of calcium carbonate. Thus:

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2.$$

Estimate the calcium bicarbonate in the water by titration.

Estimate the alkalinity of the water after boiling and filtering.

If there is any alkalinity after boiling to what can it be due?

(*k*) Calcium bicarbonate may also be removed from water by adding lime (calcium hydroxide) when the following reaction occurs:

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O.$$

To a large volume of tap water add a definite volume of lime water so that the water colours phenolphthalein paper pink. Allow the mixture to stand over night in a closed bottle, or filter rapidly after the addition of a little fuller's earth, which aids the removal of the sediment. Find out by titration how much lime is left in solution and calculate from your result how much calcium bicarbonate was present in the tap water.

(*l*) The permanent hardness of water is that hardness which remains after boiling, and it is due to salts of lime which are mainly the chloride and sulphate. If such water be boiled with sodium carbonate calcium carbonate is precipitated, and neutral sodium salts are formed. The alkalinity due to the sodium carbonate thus diminishes. It is unlikely that the sample of water would contain more than one part of lime salt per thousand of water.

To estimate the permanent hardness, add an excess of sodium carbonate, boil for five minutes, filter, and titrate back with a strong acid, using a suitable indicator.

Express both temporary and permanent hardness as mgs. CaO per litre.

(*m*) Given a mixture of sodium hydroxide and ammonium hydroxide, determine the proportions of the two.

(i) Titrate the mixture, using methyl orange. Titrate again after boiling away the ammonia.

(ii) Estimate the ammonia by distilling the mixture into a measured volume of a mineral acid solution. Be careful that no sodium hydroxide is carried over with the steam. Such mechanical carrying over of substances not in themselves volatile is called priming.

(*n*) Given a solution containing ferric chloride and a standard solution of sodium hydroxide, estimate the percentage of iron by titration. Report on the disadvantages of this method.

(*o*) Estimate the percentage of sodium carbonate in a mixture of sodium carbonate and hydroxide by titration before and after the addition of barium chloride, using methyl orange as indicator.

(*p*) Estimate the percentage of barium in a solution of barium chloride by means of a standard solution of sodium carbonate.

CHAPTER XIX

Volumetric Analysis (continued) Operations involving Oxidation and Reduction

88. Theory

It has been pointed out in the previous chapter that the substance **formic acid** contains only one hydrogen atom in the molecule replaceable by metals, and therefore if we wish to make up a standard solution we use one gram molecular weight of this substance dissolved in a litre of water. But it is easy to show that formic acid in the presence of an oxidising agent is rapidly oxidised to carbonic acid, and in this process both hydrogen atoms are oxidised thus:

$$H.COOH + O = H_2CO_3 \text{ or } H_2O + CO_2.$$

Or, since atoms of oxygen cannot exist free, we write by convention:

$$2H.COOH + O_2 = 2H_2CO_3 \text{ or } 2H_2O + 2CO_2.$$

Since formic acid so readily removes oxygen from various substances, it might well be used as a measure of the oxygen they contain, and we might titrate the amount of oxygen in various compounds dissolved in water, using a solution of formic acid as our standard.

If we adopt the same plan as we did in acidimetry we should make up a solution of formic acid such that there was one gram of available hydrogen per litre. For this purpose it will be clear we require to take only half a gram molecular weight of formic acid per litre, since the two atoms are available for oxidation, although only one of them is displaceable in titration with alkalis.

Sulphites likewise are **reducing agents**, for they are readily oxidised to sulphates; thus, for example:

$$2Na_2SO_3 + O_2 = 2Na_2SO_4.$$

We observe that one molecule of Na_2SO_3 combines with one atom of oxygen, and is thus equivalent to two atoms of hydrogen.

Thus we would need to take one half of a gram molecular weight of sodium sulphite for every litre of water to make a standard solution.

Consider now the case of **ferrous sulphate**, which is oxidised to ferric sulphate by many oxidising agents in the presence of sulphuric acid. The oxidation is represented by the equation:

$$2FeSO_4 + O + H_2SO_4 = Fe_2(SO_4)_3 + H_2O,$$
$$\text{or } 4FeSO_4 + O_2 + 2H_2SO_4 = 2Fe_2(SO_4)_3 + 2H_2O.$$

Thus here, one atom of oxygen oxidises two molecules of ferrous sulphate, and to make a standard solution we should have to take one quarter of a gram molecular weight of ferrous sulphate per litre of water.

In short, for every particular reducing agent we must know how many atoms of oxygen take part in the oxidation in order to calculate the weight to be taken for our standard solution. In each case we will take, per litre of water, that weight of reducing agent which directly or indirectly is equivalent to one gram of hydrogen.

Consider now the matter from the other side. How shall we make up standard solutions of **oxidising agents**? **Hydrogen peroxide** would be the simplest example. There is one oxygen atom available for oxidisations. Thus with formic acid we should have the reaction:

$$H_2CO_2 + H_2O_2 = H_2CO_3 + H_2O.$$

Since each molecule of H_2O_2 is able to oxidise two atoms of hydrogen we must, to make a standard solution, take one half a molecular weight in grams per litre.

Many oxidising agents are complex in composition being formed from oxides of polyvalent metals. For example, **potassium permanganate** $K_2Mn_2O_8$ may be thought of as an union of K_2O and Mn_2O_7. In the presence of sulphuric acid, the higher oxide tends to pass to the more stable lower oxide which combines with the acid to form manganous sulphate. This change is very slow unless some reducing agent is present, but provided there is some substance to remove the oxygen the change is rapid. Thus in the presence of sulphuric acid and a reducing agent we have the following changes:

$$(K_2O.Mn_2O_7) + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5O + 3H_2O.$$

In order to write $5O_2$ instead of 5O, it is usual to double the equation, but for purposes of calculation this is only confusing and is not necessary. As written in the first instance the matter is extremely simple, and it is clear that since one molecule of potassium permanganate contains five atoms of oxygen available in oxidations, we need to take one-tenth of a gram molecular weight to make our standard solution equivalent to one atom of hydrogen per litre.

89. A simple way of writing equations for volumetric calculations

If the student will get into the way of expressing the chemical change by writing oxides and ignoring the acid part of the salts, he will probably find the writing of equations very simple. Should it be necessary to present the full equations, it is merely requisite to put acid radicles in the place of all reacting oxygen atoms. Thus, with potassium permanganate and ferrous sulphate, we write down the oxides used and formed thus:

$$(K_2O.Mn_2O_7) + 2FeO \mid K_2O + 2MnO + Fe_2O_3.$$

Each permanganate molecule yields five, and every two iron oxide molecules require one atom of oxygen, therefore we need to take for the equation ten of the ferrous oxide for one of the permanganate, thus:

A. $$(K_2O.Mn_2O_7) + 10FeO = K_2O + 2MnO + 5Fe_2O_3.$$

Now write the oxides as sulphates, for only in solution will the oxidation take place. We have, then, substituting SO_4 for O, in the oxides.

B. $$K_2Mn_2O_8 + 10FeSO_4 \mid K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3.$$

We have now on the left ten and on the right eighteen SO_4 groups, and to balance the equation we must place eight molecules of H_2SO_4 on the left. These eight molecules of H_2SO_4 will yield eight molecules of H_2O, which therefore go to the right. The full equation is therefore

C. $$K_2Mn_2O_8 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O.$$

This last equation is of academic value only, the practically useful representation of the essence of the change being the oxide equation A.

90. Titration by means of potassium permanganate

With permanganates the end point of the reaction is indicated by the fact that the permanganate colour persists, for this colour is so intense that the slightest excess is readily visible.

Some substances such as ferrous salts are readily oxidised in the cold; others require a higher temperature in order that oxidation may proceed rapidly.

A. **Titration in the cold.**

Given N/10 potassium permanganate solution, estimate the weight of iron in each cc. of a ferrous sulphate solution.

Procedure.

Measure accurately 1·00 or 2·00 cc. ferrous sulphate solution into a tube flask or beaker. Add one drop of concentrated H_2SO_4 and run the permanganate solution into the iron solution until a faint pink remains definitely for a minute, even after shaking.

1 cc. N/10 $K_2Mn_2O_8$ = ·0056 grm. Fe.

Theory

In oxidations we have

$$2FeO + O = Fe_2O_3.$$

Thus 2FeO is equivalent to O.
FeO ,, H.

B. **Titration in hot solution.**

Given an N/10 solution of potassium permanganate, estimate the amount of oxalic acid present in each cc. of a solution.

Procedure.

Measure accurately a volume of the oxalic acid solution, say 1·00 cc., add 1 drop of H_2SO_4 conc., warm the solution nearly, but not quite, to the boiling point; about 70–80° C. is sufficient. Run in the permanganate solution drop by drop until a permanent pink remains for several minutes even after thoroughly shaking.

1·00 cc. N/10 $K_2Mn_2O_8$ = ·0045 grms. oxalic acid ($H_2C_2O_4$).

Theory

The oxidation of oxalic acid may be written:

$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} + O = 2CO_2 + H_2O.$$

A decinormal solution of oxalic acid contains, therefore, $\frac{90}{10}$ grms. per litre, or 1·00 cc. = ·0045 grms. $H_2C_2O_4$.

91. Titration by means of potassium dichromate

Potassium dichromate or chromate in the presence of an acid is another example of an oxidising agent, the higher oxide, chromic oxide or chromic acid, as it is often called, being the agent concerned. The essence of the change may be expressed as follows:

$$2CrO_3 = Cr_2O_3 + 3O.$$

Thus every CrO_3 molecule is equivalent to six atoms of hydrogen.

Of potassium dichromate we require a sixth and of the chromate a third of a molecule for every litre of a standard solution.

With permanganates the end point of the reaction is indicated by the fact that the permanganate colour persists, for this colour is so intense that the slightest excess is readily visible. With the dichromate on the other hand, an end point would not be obvious, and some special indicator must be used. It is usual to titrate the excess of dichromate by means of ferrous sulphate, and to use potassium ferricyanide as an indicator.

The operation is carried out as follows:

Ferrous sulphate is run in from a burette until the yellow colour of the dichromate or chromate has nearly disappeared and given place to the green colour of the chromium salt; from time to time a drop of the solution is removed on a glass rod and added to a drop of potassium ferricyanide on a white tile. So long as only ferric and chromium salts are present only a brown colour will be produced by mixing the drops, but as soon as any trace of ferrous salt is present a blue colouration (Prussian blue) will be obvious. This colour indicates, therefore, that all the oxidising agent has been reduced.

Note.—Estimation of various organic substances by potassium dichromate (chromic acid).

Many organic substances can be estimated by oxidation by potassium dichromate, in the presence of a mineral acid, usually sulphuric acid. The oxidation of a carbohydrate, for example, may be written thus:

$$XC.H_2O + XO_2 = XCO_2 + XH_2O.$$

Knowing the composition of the substance, it is easy to calculate how many atoms of oxygen will be required for oxidation, and we have seen that each molecule of potassium dichromate can supply three atoms of oxygen, for the purpose. (See the later chapters on organic chemistry.)

92. Titration by means of iodine

The halogens are other examples of oxidising agents, and iodine, especially, is used in volumetric analysis. Arsenites, sulphites, thiosulphates, sulphides, and many other reducing agents may be titrated by means of a solution of iodine, which has the advantage like potassium permanganate that the substance is its own indicator, for it is easy to see that the brown colour of an iodine solution has been discharged by the reducing agent. Since, however, iodine gives a most intense blue colour with a solution of starch it is usual to employ this substance as an indicator in iodine titrations, for this makes possible a greater accuracy in the reading of the end point.

The following are some examples of oxidation by iodine:

$$H_2S + I_2 = 2HI + S.$$
$$H_2SO_3 + H_2O + I_2 = H_2SO_4 + 2HI.$$
$$As_2O_3 + 2H_2O + 2I_2 = As_2O_5 + 4HI.$$

A weak alkali such as sodium bicarbonate must be added to neutralise the hydriodic acid as it is formed, otherwise it will decompose and the end point of the titration will not be sharp.

With thiosulphates a curious reaction occurs, giving rise to a substance called a tetra-thionate thus:

$$2H_2S_2O_3 + I_2 = H_2S_4O_6 + 2HI.$$

As before, the reaction must be carried out in faintly alkaline solution.

Procedure.

Measure accurately a volume, say 1·00 cc. of the solution to be estimated, add about 20 mg. of $NaHCO_3$ and 1 drop of a freshly prepared starch emulsion. Run in the solution of iodine until the deep blue colour of the iodine starch compounds remains for half a minute, even after shaking.

1·00 cc. N/10 iodine is equivalent to

0·0017 grms. H_2S.
0·0032 ,, SO_2.
0·00495 ,, As_2O_3.

CHAPTER XX

Volumetic Analysis (continued) Process involving Precipitation

93. Estimation of chlorides by silver and vice versa

If we add gradually a solution of one salt to a solution of another it often happens that a precipitate is formed which is so insoluble that no trace of the added salt can be detected in the solution until the whole of the other salt has been changed. For example, if we add silver nitrate to a solution of sodium chloride all the silver is precipitated as chloride, and none of it can be detected in solution so long as any chloride remains there. The moment any silver appears in solution we may be quite sure that all the chloride has gone. If, then, we possessed a solution of silver of known concentration we could estimate the amount of chloride present in another solution by gradually adding the former to the latter until free silver was present in the solution. But how are we to tell when free silver is present? We need some indicator. A soluble chromate such as potassium chromate has been found to answer the requirements of the case.

Chromic acid is a weak acid compared to hydrochloric acid, so that if a soluble silver salt is added to a solution containing chlorides and chromates the chloride first reacts with the silver to form silver chloride, and no silver chromate is formed. A further reason for the formation only of silver chloride is that silver chloride is more insoluble, and it is the rule that the most insoluble substance is first precipitated; probably this latter is the most important of the two reasons given. As soon, however, as all the chlorides have been precipitated any added silver will react with the chromate and give a precipitate of silver chromate which is readily recognised by its red colour. Unfortunately the red precipitate of silver chromate as has been mentioned is a weak combination, and consequently it is decomposed by acids even in dilute solution. Silver and chlorides can only be titrated in the manner described above when the solution is about neutral. This, however, is a very useful method of estimating chlorides in specimens of tap water, river water, etc., and the method has many applications, for example, in deciding as to whether water has been contaminated or whether spring water comes from the sea or from a neighbouring river, and so on.

You must be supplied with a solution of silver nitrate as standard (N/20 will be sufficiently concentrated), or you must dissolve up a definite weight of silver nitrate, or metallic silver. In the latter case the silver must be dissolved in nitric acid and the solution evaporated on the water bath to expel all free acid.

It is always better, if time permits, to make up a solution of some simple fraction of normality such as N/10 or N/20, for in such a way you avoid continual factor corrections which calculations consume more time than the actual titrations, and it must be remembered that the outstanding advantage in volumetric analysis as compared to gravimetric work is the saving of time.

Chlorides in tap water

Procedure.

Take about 20 cc. of the water. If the water is alkaline, neutralise by a drop or two of acetic acid. Add a drop of potassium chromate as indicator. Run in the silver solution until a permanent pink colour is obtained. If less than 1·00 cc. of silver solution is required, add more tap water, and continue the titration.

1 cc. $AgNO_3$ N/20 is equivalent to ·002925 grm. NaCl.

Caution in silver titrations

Do not forget that silver salts are affected by the light. Titrations should be carried out in a dull light, and silver solutions when not being used should be kept in the dark.

Recovery of silver from residues

Silver is a valuable metal, and must be used with care. It is here that it becomes especially of advantage to titrate by means of a microburette.

All silver residues should be kept in a special residue jar, and at the end of the term the silver should be recovered.

94. The titration of silver solutions by (sulphocyanides) thiocyanates

The advantage of this method depends upon the fact that silver sulphocyanide or thiocyanate (the words are synonymous) is insoluble in dilute nitric acid. There is, therefore, no need to neutralise the solution before titration as in the method previously described. It follows, however, that chromates cannot be used as indicators, but this does not matter, because sulphocyanides which give with ferric salts a deep red colour, can be used instead. If, therefore, a drop of ferric chloride is added to the silver solution and a solution of potassium sulphocyanide is run in, there will appear, as soon as all the silver is precipitated, a deep red colour due to the ferric sulphocyanide. This colour will not appear so long as any silver remains in solution because of the great insolubility of silver sulphocyanide.

1. Prepare 25 or 50 cc. of a N/20 soln. of KCNS or NH_4CNS.
 The crystals of the sulphocyanide must be dry and white. A yellow colour indicates that there has been some decomposition with the liberation of sulphur. The solution should not be kept in the sunlight.
2. Titrate the sulphocyanide solution against the silver nitrate solution previously prepared.
 Take 1·00 cc. of silver nitrate solution, add 5 cc. distilled water in a small white dish, add one drop of a dilute solution of ferric chloride, and run in the sulphocyanide solution until a red colour remains permanently in the solution.
 Each cc. N/20 sulphocyanide corresponds to 0·005394 grm. silver.

The indirect estimation of chlorides by sulphocyanides

If we wish to estimate chlorides in the presence of acids our best plan is to add an excess of silver solution and filter off the precipitate of silver chloride. We can now estimate the amount of silver in the filtrate in the manner described in the previous exercise. By difference we can deduce the amount of silver which has been precipitated as chloride, and hence the amount of chloride present.

This method is particularly useful if we wish to estimate chlorides in mixtures containing phosphates, for silver phosphate is not precipitated in the presence of even dilute nitric acid.

1. Estimate the amount of chlorine in the form of chloride present in the sample of water supplied to you
2. The mixture contains calcium phosphate and magnesium chloride Estimate the amount of chlorine present as chloride.

95. The estimation of calcium by precipitation as oxalate, and titration with permanganate

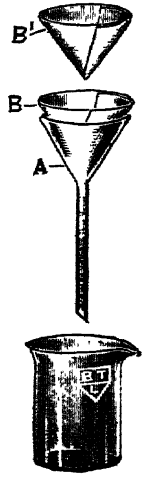
When oxalic acid is added to a solution of a calcium salt in the cold the precipitate of calcium oxalate is often so finely divided that it yields a colloidal suspension which is exceedingly difficult to filter. But if the precipitation is carried out by adding the oxalic acid to a solution which has been brought to the boil, the precipitate aggregates into larger crystalline masses which readily settle, and may be filtered with ease. The precipitate of calcium oxalate is insoluble in dilute acetic acid, and advantage is taken of this fact in that we add a little acetic acid before precipitation, and thus should any carbonate or phosphate be present in the solution there is no chance of it being precipitated on boiling; likewise traces of such metals as magnesium are not precipitated, because their oxalates are soluble in acetic acid.

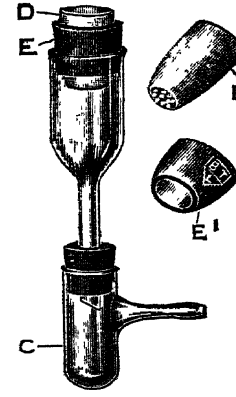
The precipitate of oxalate may be filtered away by means of paper, or better by means of asbestos on a Gooch crucible (see Fig. 14), or the excess of oxalic acid may be estimated in the filtrate as follows:

Procedure.

Take a definite volume say 2·00 cc. of a solution of a calcium salt in a small beaker, add 10 cc. of distilled water and one drop of acetic acid, bring the solution to the boil, and add a drop at a time sufficient oxalic acid of known strength N/20 to precipitate all the calcium. A crystalline precipitate should form. Cool and transfer the solution to a small graduated 50 cc. flask, and make up to the mark with distilled water. After thoroughly shaking the flask to ensure proper admixture, filter and titrate a definite volume of the filtrate to which a few drops H_2SO_4 conc. has been added against a standard solution of potassium permanganate. In this way you know how much oxalic acid has not been precipitated, and hence you can calculate the amount of oxalic acid which corresponds to the calcium present in the solution.

If instead of titrating the excess of oxalic acid in the filtrate you are required to titrate the oxalic acid in the precipitate, you proceed as follows :





(*a*) **If on paper,** wash thoroughly with boiling water until the filtrate is free from oxalic acid. Wash the oxalate precipitate into a beaker by means of a spray of hot water, add a few drops of H_2SO_4 conc., and titrate with permanganate.

(*b*) **If on asbestos,** which is by far the better way, wash with a little water, remove the asbestos to a beaker, wash the

crucible over the beaker, add a few drops of H_2SO_4 conc., and titrate with permanganate.

The danger with the paper filtration method is that a trace of paper may be removed with the calcium oxalate, and on titration with permanganate this material (cellulose) will be oxidised also and give a false result. Moreover, the paper filtration method is very tedious.

96. The indirect estimation of organic acids by means of calcium

Organic acids may be estimated by neutralisation with chalk, filtering the solution and estimating the calcium in solution. From this figure you know at once the corresponding weight of the organic acid present provided you know what the acid is.

CHAPTER XXI

The Detection of the Elements in an Organic Substance

97. Proximate and ultimate analysis

Analysis with a view to recognising the elements present may be proximate or ultimate.

By **proximate analysis** we mean that the material is converted or separated into one or more substances which can be identified, but these substances are not necessarily simple. The essential point however, is that it should be possible to recognise them with ease.

Milk, for example, is a mixture of water, fat, protein, carbohydrate, salts, and so on. A proximate analysis consists in separating these, if possible, without destroying them. Sometimes it may be requisite to destroy one constituent in order to separate the other. For example, in separating fat from milk, while it is possible to extract the fat from milk by dried ether, yet it is easier first to heat the milk with a mineral acid to destroy the albuminous film around the fat globules. The fat then floats to the surface, and may be readily measured.

Testing for various complex substances by reagents with which they form characteristic reactions is also proximate analysis. For example, to identify starch we add a drop of iodine and the blue colour obtained tells us that we are dealing with starch more easily than can any ultimate analysis.

Ultimate analysis is practically reserved for cases where we meet some unknown substance, i.e. a substance which after ordinary proximate analysis fails to reveal its identity. Ultimate analysis is, indeed, generally the last resort. It is a destructive method. Remember, therefore, that you should first do everything possible to find out what the substance is before you destroy even the least fragment of it. It is much more credit to you if you can say what the substance is, and at the same time return the original sample almost untouched. The more in fact you practise identifying the substance by purely physical means which do not destroy the material the more surely will you master the idea of analysis.

98. Tests for the elements in organic compounds

Carbon

(*a*) **The evolution of CO_2 sometimes CO, on heating,** or on decomposition by other means.

(*b*) **Deposition of carbon when combustion is incomplete.** This applies particularly to substances containing but little oxygen, and a great proportion of carbon, such as fats, and many hydrocarbons.

(*c*) **Carbonisation resulting from action of mineral acids,** due generally to the removal of water. This occurs, especially with carbohydrates.

H_2SO_4 conc., is the most suitable acid for the purpose. Only one drop should be employed, and heating, if any, should be very carefully carried out.

(*d*) **Reduction of oxidising agents.** This is not absolute proof of carbon, but it is valuable evidence.

Mix one drop of a solution of the substance in water with one drop of N. potassium dichromate ; add one drop of H_2SO_4 conc. ; a change of colour to yellow or green is practically proof that the substance contains carbon. Certain inorganic substances such as iron salts also reduce, but they will reduce the dichromate even with very dilute acid, and may be thus distinguished Similar remarks apply to potassium permanganate

Hydrogen

(*a*) **Formation of water on cold surface** held near the burning material.

(*b*) **Higher temperature of the flame.** Substances rich in hydrogen give less luminous flames, because the combustion is at a higher temperature.

Thus a substance which burns well, but does not readily give a deposit of carbon on a cold surface, may be inferred to contain relatively more hydrogen than another substance which does show carbon deposition, provided, of course, the conditions of the experiment are approximately the same.

(*c*) **Reduction of oxidising agents at a low temperature.** When reduction takes place in the cold or with gentle heating only, it is most likely due to the hydrogen and not the carbon present.

The same remark applies to reduction in neutral solutions, or solutions only slightly acid or alkaline, especially when the reduction is powerful.

For example, if formalin (formaldehyde) is gently warmed with a solution of a cupric salt, metallic copper is deposited. Such an intense reduction without the application of much energy from without indicates the presence of hydrogen in the substance.

Similarly grape sugar, when boiled with alkaline copper solutions, reduces them yielding a red precipitate of cuprous oxide, but cane sugar does not. These sugars contain about the same proportion of carbon, but in grape sugar the hydrogen is more active. In this case an important fact is not only how much hydrogen is present, but whether the hydrogen is free to react.

Nitrogen

(*a*) **Formation of ammonia, amines, pyridine, etc., on heating or burning the material.** All these volatile substances have a characteristic smell. A smell which recalls burning leather, horn, or feathers.

(*b*) **Formation of NH_3** on heating the substance with strong hydroxides, NaOH, $Ca(OH)_2$, etc. (A mixture of these two hydroxides is called soda lime.)

A few specks of the organic material should be thoroughly mixed with about ten times its amount of soda lime, and the heating be gradually applied. The ammonia may be recognised by the odour or by litmus, turmeric or other indicator.

(*c*) **The formation of a cyanide.**

A small pellet of metallic sodium about the size of a pea is flattened out with a pocket knife, and upon it some of the organic material is spread. The metal is then rolled up so as to enclose the organic substance and placed in a hard glass tube. Heat is applied gently, the tube being held well away from the operator, as a sudden explosive expulsion of the contents of the tube sometimes occurs. The sodium melts, and there is an ignition of the material. Various changes occur, the result of which is the formation of sodium cyanide, NaCN. To recognise the cyanide the quickest way is to change it to ferrocyanide. To do this add a crystal of ferrous sulphate, and with care a drop or two of water, and allow the mixture to stand for five minutes. The reaction is a little slow. Now add a mineral acid (HCl) to neutralise the carbonates which are also formed, and the excess of sodium hydroxide which is present, and then add a drop of ferric chloride, which with the ferrocyanide already formed yield a blue colour (Prussian blue).

The reactions are.

Fusion.

Organic substance $(C.H.N)+Na=NaCN+H$.

(The escaping hydrogen would ignite in the presence of air.)

Addition of ferrous sulphate solution.

$$6NaCN+FeSO_4=Na_4Fe(CN)_6+Na_2SO_4.$$

The Prussian blue test for ferrocyanide depends upon the formation of ferric ferrocyanide.

$$3Na_4Fe(CN)_6+4FeCl_3=Fe_4[Fe(CN)_6]_3+12NaCl.$$

Sulphur

(i) **Direct interaction with lead acetate.**

Heat a speck of the material with a few drops of a concentrated solution of NaOH and a drop of lead acetate. A blackening indicates sulphur.

(ii) **Reduction to sulphide.**

Fuse with sodium carbonate on charcoal. Place the fused mass on a silver coin and add a drop of water. A black stain indicates sulphur. Or boil the mass after fusion with lead acetate.

(iii) **Oxidation to sulphate.**

Many organic substances contain sulphur in a form in which it is not easily made to yield the sulphide. Such compounds may be oxidised by nitric acid or a mixture of nitric and hydrochloric acid, or they may be fused with sodium carbonate and nitrate. The result in each case is the formation of a sulphate, which may be recognised by the formation of a white precipitate on the addition of barium chloride in dilute solution.

Phosphorus

In a compound phosphorus is always recognised by oxidation of the material either by a mixture of nitric and sulphuric acids or by fusion with sodium carbonate and nitrate. The solution of the residue after oxidation is boiled with nitric acid and ammonium molybdate, when a characteristic bright yellow precipitate of ammonium phospho-molybdate is obtained.

This precipitate is readily soluble in a solution of ammonium hydroxide, from which solution it may be reprecipitated by nitric acid. Also from this solution the phosphate may be conveniently precipitated by the addition of magnesium chloride solution and excess of ammonium hydroxide. Ammonium magnesium phosphate is formed, which is readily recognised under the microscope by the feathery form of its crystals

Halogens

(*a*) A copper wire dipped in the organic material and then held in the flame yields a more vivid green than when the material is devoid of halogens. This is due to the fact that the copper halogen salts are more volatile than other copper compounds.

(*b*) The residue after fusion with sodium carbonate contains chloride, etc.

(*c*) Heating with lime.

This is carried out in a hard tube as a high temperature is required to decompose many halogen compounds. After cooling, the alkali is neutralised with nitric acid and the halogen recognised by precipitation with silver nitrate

CHAPTER XXII

The Examination and Provisional Classification of some naturally occurring Organic Substances

99. Preliminary Examination

Collect a number of organic substances, or substances which you suspect to be organic, and study them with respect to the following particulars: **Appearance** (examine also under the microscope), **specific gravity, solubility** in water, and other solvents, **melting point, effect of heat** in a closed and open tube, **reaction** towards litmus paper and other indicators, **effect of heating with dilute acid.** From the results of your examination answer the following questions with regard to each substance:

(1) Is it crystalloid or colloid?
(2) Do you think it has a high or a low molecular weight?
(3) Is it a neutral, an alkaline, or an acid substance?
(4) Does it contain much hydrogen?
(5) Does it contain much oxygen?
(6) Do you think the hydrogen and oxygen exist in the proportion in which they exist in water?
(7) Does the substance contain nitrogen?
(8) Is mineral matter present?
(9) Are you dealing with a pure substance or a mixture?

All these questions may be answered after applying the tests described above, and you require in all only a few specks of material, provided you carry out your tests in the proper order. Remember to carry out first such tests as do not destroy the material.

100. Organic substances easily obtained

The following are examples of some substances which are easily obtained: Coal gas, coke, wood, paper, starch, gum, sugar, vegetable oil, mineral oil, animal grease, beeswax, resin, tar,

candle grease, naphtha, camphor, turpentine, spirits of wine (methylated spirits is very little different, and will serve most of the purposes of spirits of wine), vinegar, oxalic acid, tartaric acid, cream of tartar, gelatine (glue is impure gelatine), white of egg, flour, vaseline, glycerine, soap, cotton wool, india rubber, cork, ebonite, sealing wax, celluloid, bone, cartilage, meat, benzene, benzine, aniline, ether, chloroform.

These materials or substances have been purposely enumerated without regard to classification in order that the student may have the exercise of arranging them into groups. (A material may be a mixture, but a substance must be a single material, though it is still called a substance even when not quite pure ; ideally, however, the word substance refers to a pure thing.)

101. Provisional classification

The materials should be arranged into the following groups :

(1) Mixtures or single substances.

(2) Crystalloid or colloid.

(3) Simple or complex.

(4) Hydrocarbon, carbohydrate, fat, nitrogenous substance.

Under each heading in (4) we would include allied substances ; thus candle grease comes under fats, glycerine under carbohydrates and so on.

The following example may serve to help the student in his classification. The classification must, of course, be based upon the results of his own experiments.

Name of the Material	Mixture or single substance	Crystalloid or colloid	Complex or simple	Kind of group (including derivative)
Glycerine	single	crystalloid	simple	carbohydrate (deriv.)*
Egg white	mixture?	colloid	complex	nitrogenous
Oxalic acid	single	crystalloid	simple	carbohydrate (deriv.)
Candle grease	mixture?	crystalloid	medium complexity	fat. (deriv.)

* By a derivative we mean a closely allied or simply derived substance.

Later the student will be able to classify substances with greater precision, but it is of value in the first instance to be able to make the above provisional classification.

When there is uncertainty the student may place a ? after naming the most probable conclusion.

We must now consider in a little more detail upon what evidence we may undertake such a classification.

102. Is a material a mixture or a single substance

It is the physical test which must help us to decide this point, namely:

(*a*) **Microscopic examination.**

Even with the low magnification of a pocket lens you may learn much. Crystals of various forms may be seen, or there may be crystalline and amorphous substances. Different colours may be observed. Some crystals may be clear, others opaque, some may show signs of decomposition which may be highly suggestive. A polarising microscope is of great value. The material may also be examined under the microscope after treatment with a drop of a solvent. This is an excellent way of determining not only solubility of the substance as a whole, but also whether there are several substances present.

(*b*) **Solubility.**

One substance may dissolve and the other not dissolve in water. Or we may try other solvents such as methylated spirits (ethyl alcohol), benzine, chloroform, ether, or acids and alkalis dissolved in either water or alcohol.

(*c*) **Melting point.**

A sharp melting point indicates a pure substance, an indefinite melting point a mixture.

An approximate idea of the melting point may be gained by emersing in a liquid at various temperatures a capillary tube containing a speck of the material and observing on withdrawal whether the substance has melted.

An accurate measurement of the melting point is of the highest value. It is generally made as follows:

A minute speck of the material is introduced into a capillary tube, the tube is strapped to the lower end of a thermometer, and both are dipped in a liquid, which

is then gradually heated. For low temperatures water or salt solution may suffice; for temperatures much above 100° C., sulphuric acid is generally used. As this is a dangerous material phosphoric acid or glycerine may be used to replace it.

The temperature must be very gradually raised, and the fragment watched through a lens until it is seen to melt. Sometimes the work is more readily done by two, one watching the fragment, the other watching the rising thread of the thermometer.

The arrangement of apparatus is seen in Fig. 15.

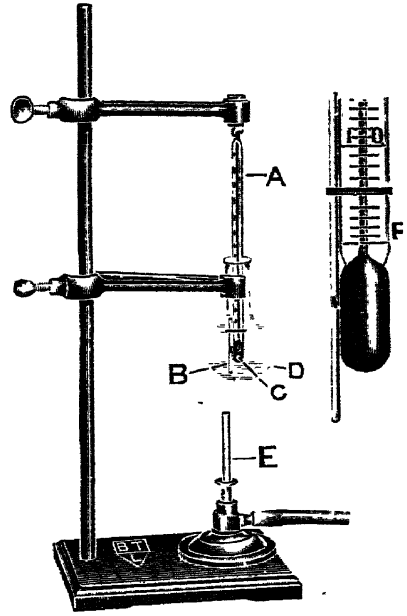


Fig. 15. "The melting point" apparatus.

A. Thermometer.
B. Bulb of thermometer dipping into liquid.
C. Capillary tube containing the substance.
D. Special resistance glass tube.
E. Micro burner.
F. Enlarged view of lower end of thermometer and capillary tube, showing the substance placed opposite the bulb.

(*d*) Boiling point.

Similar remarks apply to the boiling as to the melting point.

(*e*) **Evaporation or distillation of the material.**

It may be possible to evaporate one constituent, or to distil it in several different portions which we call fractions. In this way the several constituents of a mixture may be separated and examined. Even in a small tube with careful watching it may be possible to observe whether gentle heat brings about a separation of constituents, indicating that the substance is a mixture. But it must be understood that many substances when strongly heated decompose into components which may distil. We call this destructive distillation. Such products do not indicate that the substance is a mixture originally. They may, however, give valuable information as to the nature of the compound.

(*f*) **Recrystallisation.**

This is a most valuable art, and one which almost more than any other distinguishes the chemist from the amateur. Crystallisation, as a rule, will not occur until a considerable degree of purity has been reached, but there are certain exceptions as, for example, when you are dealing with several closely allied substances, for example, several fatty acids. This is, in reality, part of the law of isomorphism, i.e. that substances of similar chemical constitution crystallise in similar forms.

To obtain good crystals the solution must be allowed to cool slowly, and it must not be too concentrated. There are too many considerations, however, which determine crystallisation for it to be possible to enumerate them. Experience must be gained by practice. It is for this reason that the student should always examine the solubility of any substance presented to him with great care and try to prepare crystals from the substance. If a substance after recrystallisation possesses the same physical properties such as melting point, solubility, crystalline form, etc., it is good evidence that it is pure. No mixture, even of isomorphous substances, will remain quite the same after repeated recrystallisations.

Crystals tend to form at irregular surfaces, and that is why you will often see a chemist scratching the walls of a glass vessel to encourage the formation of crystals which

are slow to appear. Once started the crystals will continue to grow, and if the solution is undisturbed they may reach considerable size. The form in which a substance crystallises, however, may vary with the solvent. Crystals may also be hydrated. Sometimes a salt will crystallise better than the acid, or it may be vice versa. Sometimes, in order to start the crystallisation, a few particles of dust may be introduced, but this is seldom necessary. Sometimes the only way you can start the crystallisation is to introduce a minute crystal of the substance in question which you have obtained from elsewhere.

103. Is the substance simple or complex?

In judging this point you may be guided by the following general considerations:

(1) The simpler the substance the lower the melting point or boiling point.

Thus gases are simpler than liquids and liquids than solids, considered at the same temperature.
This rule applies with accuracy when the substances consist all of the same elements.

(2) Soluble substances are generally simple while insoluble ones are complex.

(3) Substances which can be heated without decomposition are simple; complex substances tend to decompose into simpler ones when heated.

(4) Solid substances which cannot be made to crystallise are either mixtures or very complex individuals. Simple solid substances, if they dissolve, will crystallise from solution.

(5) Crystalloids are simpler than colloids.

104. Temporary and permanent colloids

Although, however, many substances such as starch are colloids always possessing very high molecular weights (over 10·000), yet many other substances may be colloidal at one time and crystalloidal at another. A colloidal solution is really a suspension in a fluid of fine particles which may be either large single molecules or aggregates of smaller molecules; in the former case the substance itself may be described as a colloid; in the latter case the colloidal

state is so to speak accidental, and with manipulation the particles may generally be disintegrated and the substance may be made to dissolve to form a true solution or to precipitate in a truly crystalline state.

Colloidal solutions differ from mere suspensions in that they do not yield precipitates on standing. Colloidal solutions are generally recognised by an opacity, or fluorescence. They have not the clear appearance of true solutions of crystalloids.

If you decide that the substance is a colloid (not merely temporarily, but permanently, in the colloidal form), then you are certain that it is a substance of large molecular weight, and you can answer the question : "is it simple or complex ?" without even knowing the composition of the substance. But if you decide that the substance is a crystalloid you may still need to decide whether it is comparatively simple or complex.

CHAPTER XXIII

Hydrocarbons

105. Physical properties

From the specific gravity we know the molecular weight.

There are two factors making for lightness: (*a*) the smallness of the molecule, (*b*) the preponderance of hydrogen over carbon in the molecule. Thus the larger the molecule the greater will be the specific gravity, and there will be a gradual transition from gas through liquid to the solid state.

With the saturated hydrocarbons or paraffins, for example, the first three members of the series at atmospheric pressure are gases below the temperature of ice; the fourth is just liquefied by ice, after which there is a rise in the boiling point of about thirty degrees for every carbon atom added.

The following are the figures for the boiling points:

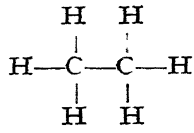
Methane	CH_4	gases below	—50°	at	atmospheric	pressure
Ethane	C_2H_6	boiling point	—45°	,,	,,	,,
Propane	C_3H_8		0°	,,	,,	,,
Butane	C_4H_{10}		37°	,,	,,	,,
Pentane	C_5H_{12}		69°	,,	,,	,,
Hexane	C_6H_{14}		98°	,,	,,	,,
Heptane	C_7H_{16}		125·5°	,,	,,	,,
Octane	C_8H_{18}		149·5°	,,	,,	,,
Nonane	C_9H_{20}		173°	,,	,,	,,
Decane	$C_{10}H_{22}$					

The student will see, therefore, that any hydrocarbon which is liquid at the temperature of the room must contain at least five carbon atoms, while if it remains liquid at the temperature of boiling water it must contain at least eight carbon atoms. The higher hydrocarbons are solid. Paraffin wax is an example of a saturated solid hydrocarbon.

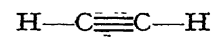
106. Chemical properties

The name paraffin implies an absence of reactivity or affinity, and hydrocarbons such as ethane C_2H_6, wherein each carbon has each of the available valencies saturated with hydrogen is certainly more stable than a compound such as acetylene. The formulae are written thus :

Ethane

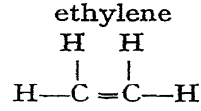


acetylene



The hydrocarbon ethylene stands intermediate between these. Its structural formula is written thus :

ethylene



Experiment.

(1) Prepare acetylene by slowly adding water to calcium carbide.

A test-tube provided with a cork and delivery tube may be used, or the gas may be collected from an acetylene bicycle lamp.

(2) Compare the properties of this gas with coal gas as follows :

Brightness of the flame. Acetylene gives a much whiter flame, because there is a greater excess of carbon over hydrogen as compared to coal gas. (See notes on tests for carbon and hydrogen in previous lesson.)

Deposition of carbon. The flame is very smoky, and the deposition of carbon is readily demonstrated.

The deposition of carbon is less obvious with coal gas.

CHAPTER XXIV

Oxidation Products of Hydrocarbons The Alcohols, Aldehydes, Acids

We may study the oxidation products either by preparing them by laboratory methods or by observing oxidation as it takes place in nature. Since natural processes take place on a large scale, and often by means of forces which we cannot ourselves direct, it is sometimes easier to obtain large quantities of materials for our study from natural sources rather than to prepare them by laboratory means. It must be understood, however, that there is no difference between a substance which is obtained in the laboratory and the substance which has the same composition and is obtained from a natural source.

107. Alcohols

The simplest oxidisation product of a hydrocarbon is an alcohol, and it is obtained by introducing one atom of oxygen into the molecule of the hydrocarbon. Thus :

Methane	CH_4	yields	methyl alcohol	CH_4O	or CH_3OH.
Ethane	C_2H_6	,,	ethyl alcohol	C_2H_6O	C_2H_5OH.
Propane	C_3H_8	,,	propyl alcohol	C_3H_8O	C_3H_7OH.

As it is difficult for the student at this stage to introduce atoms of oxygen into hydrocarbon molecules it is best for him to study the properties of the alcohols upon specimens which he can obtain from natural sources. Methyl alcohol is obtained from the distillation of wood, and is hence called wood spirit ; ethyl alcohol is obtained by fermentation of sugar in making wine or beer ; it is called spirits of wine. These two substances are readily obtained Methylated spirits is a trade name for impure spirits of wine. It was once a mixture of ethyl and methyl alcohol, the latter being added to prevent the use of the substance for drinking purposes. Nowadays, however, methylated spirits often contains no wood spirit. Other substances are added instead.

108. The preparation of ethyl alcohol by fermentation of sugar

In a 10 or 20 cc. flask introduce 0·2 gram of cane sugar. Add 5 or 10 cc. of water (tap water) and 0·1 gram of brewer's yeast. Set the flask aside at a temperature of about 25° for 24 hours. Prove that the gas evolved is CO_2.

Distil the fluid until about one half has been removed. The distillate must be collected either by passing the steam into a condenser, or by allowing the steam to bubble into a test-tube containing ice.

The distillate will be found to contain alcohol.

The arrangement of distilling apparatus is seen in Fig. 16.

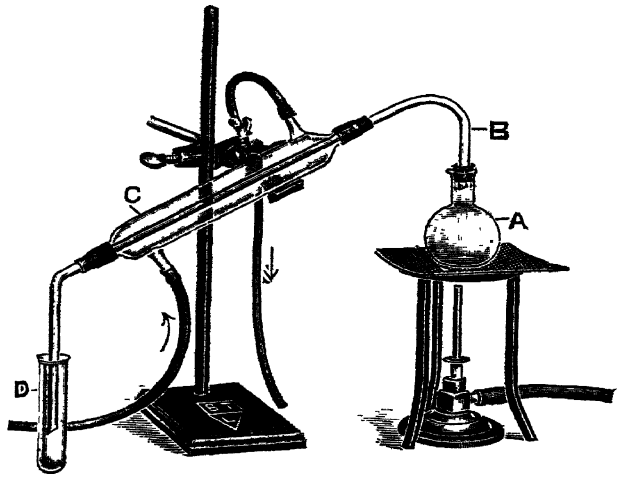


Fig. 16. Micro Distillation apparatus.

A. Flask (about 25 cc. capacity).
B. Tube leading hot vapours through condenser.
C. Water-cooled condenser.
D. Tube for receiving distillate.
The arrows show the direction of circulation of the water.

109. (*a*) The formation of halogen derivatives of hydrocarbons

The iodoform test.

To a few drops of the alcohol solution add a drop of NaOH conc., add drops of dilute iodine solution until the solution is just permanently yellow. Warm the mixture. The solution turns a deeper yellow and has a very characteristic odour of iodoform. The test is not absolutely specific for ethyl alcohol, as other closely allied substances give the reaction, but methyl alcohol will not give the test. You can say from the test that there is some substance of at least two carbon atoms present, which is probably ethyl alcohol. Iodoform has the formula CHI_3.

By this test you have therefore converted the alcohol into an iodine derivative of a hydrocarbon, and this shows you that the alcohol itself must also be a derivative of a hydrocarbon.

The reaction between alcohol and iodine would be represented as follows:

$$CH_3CH_2OH + 5I_2 + H_2O = CHI_3 + CO_2 + 7HI.$$

This is an oxidation.

But the hydriodic acid readily decomposes and liberates nascent hydrogen, which would cause the reversal of the change. To prevent this, sodium hydroxide or other alkali is added which neutralises the hydriodic acid.

The conversion of alcohols into iodides or iodine derivatives is a very general reaction characteristic of all alcohols. The simplest iodine derivative obtainable from ethyl alcohol would be ethyl iodide. C_2H_5I. Bromides and chlorides are likewise readily obtained. The chloride corresponding to iodoform is called chloroform, a most important anaesthetic.

110. (*b*) The formation of esters. Condensation

To a drop of ethyl alcohol add a drop of concentrated acetic acid and a drop of concentrated sulphuric acid. Warm gently. Observe the odour. The characteristic fruity smell is due to ethyl acetate which has been formed.

$$C_2H_5OH + CH_3COOH = CH_3COOC_2H_5 + H_2O.$$

The reaction is possible, because of the attraction of sulphuric acid for water.

This is esterification, and it is a particular case of the process called condensation, namely, the joining of two or more molecules together by the elimination of water.

When a mineral hydroxide is mixed with an acid a salt results. In this reaction water is formed by the union of the OH′ group of the alkali with the H· of the acid to form H_2O. The reaction takes place instantaneously with strong acids and alkalis because they are already ionised; the positive H· ions or free atoms attract the negative OH ions (free hydroxyl groups), and water is readily formed by their union. The remaining parts of the molecules or ions unite to form a salt or remain free in solution as the ions of the salt. But with alcohols the hydroxyl group is not free like the hydroxyl ion, and therefore it does not readily unite with

hydrogen ions to form water, and so lead to the formation of salts. If, however, we add some material which will absorb or combine with water as, for example, dry HCl, H_2SO_4, we may cause the gradual removal of the water formed by the union of the OH′ of the alcohol with the H· of the acid. This process is called condensation. We have then quite an analogy between the formation of inorganic salts and organic salts. These organic salts we call esters.

Repeat the above experiment, using other alcohols and acids. For example, formic, propionic, butyric, benzoic, and salicylic acids, and methyl, amyl alcohols.

It is not essential that the student should at this stage know the exact composition of these acids or alcohols ; the point for him to grasp is that any acid and alcohol together yield an ester under appropriate conditions, and that esters are generally volatile substances of fruity odour.

The odours of many fruits and other parts of plants are due to naturally occurring esters.

111. The effect of oxidising agents upon alcohols

(*a*) Oxidation by free oxygen. (*Dry combustion*)

Burned in excess of air, alcohols yield water and carbon dioxide, but when burned with insufficient supply of air various products may arise. Most carbon compounds when burned in insufficient supply of air yield carbon monoxide instead of carbon dioxide, and similarly when substances are oxidised in solution they yield products of various degrees of oxidation according to the amount of available oxygen in the solution.

(*b*) Oxidation in solution. (*Moist combustion*)

To 2 drops of N potassium dichromate add 2 drops of concentrated sulphuric acid. Add one drop of about 1 per cent. ethyl alcohol solution ; note the change of colour to yellowish brown. Add a second drop of the alcohol solution, the colour changes to green. The chromic acid is gradually reduced to chromium oxide, which in acid solution forms the chromium salt. This method can be used to estimate alcohol in solutions. It is the most accurate method available for this purpose, provided no other substance is present which may also be oxidised.

Oxidation in solution is not so vigorous as in the dry state, because the temperature is lower, and therefore it is not as a rule the whole of the molecule which is oxidised, but only the end of the molecule or the part of the molecule which is already partly oxidised. For example, in the presence of excess of chromic oxide (chromic acid) ethyl alcohol is oxidised in aqueous solution to acetic acid, not to carbonic acid, thus:

$$CH_3CH_2OH + O_2 = CH_3COOH + H_2O.$$

Every molecule of available oxygen is able to convert one molecule of alcohol into acetic acid. In this oxidisation it is only the $—CH_2OH$ group which is attacked; the CH_3 group, when attached to a carbon atom, is untouched. This is a general rule for oxidation with chromic acid in solution, viz., the CH_3 group, together with the adjoining carbon atom, yield acetic acid, the other carbon atoms oxidise to CO_2. In the case of methyl alcohol, which has only one carbon atom, carbon dioxide alone is formed thus:

$$2CH_3OH + 3O_2 = 4H_2O + 2CO_2.$$

It is thus easy to distinguish methyl from ethyl alcohol by oxidisation with chromic acid. The smell of acetic acid is readily recognised in the one case, but not in the other, and CO_2 is produced in the one case, but not in the other. With propyl alcohol, in accordance with the above rule, we obtain, therefore, a mixture of acetic acid and carbon dioxide. The carbon dioxide is recognised by the effervescence of the solution, or it may be passed into lime water. The reaction would be represented as follows:

$$2CH_3CH_2CH_2OH + 5O_2 = 2CH_3COOH + 2CO_2 + 4H_2O.$$

Observe that more than twice as much oxygen is required to oxidise propyl alcohol as was required for ethyl alcohol.

Repeat the above experiment with methyl alcohol, and observe that no acetic acid is formed.

112. The quantitative estimation of alcohol

(*a*) Take 0·5 cc. of N. potassium dichromate and add 0·5 cc. concentrated sulphuric acid. Add to the mixture drop by drop the dilute solution of alcohol, adding not more than 0·5 cc. in all. Keep the solution hot for five minutes by holding the tube in boiling water.

(*b*) Add cold water to the tube, and wash the solution into a beaker or white porcelain dish and find out how much chromic acid remains unreduced by titration with a solution of ferrous sulphate. The ferrous sulphate should be about N/50. (See Ch. XIX., Section 91.)

(*c*) From the amount of chromic acid reduced by the alcohol the amount of alcohol present is readily calculated from the equation given above.

1 cc. $N.K_2Cr_2O_7 = 0{\cdot}0115$ grm. C_2H_5OH.

113. Partial oxidation of alcohols in solution

Just as in combustion in air, we obtain CO instead of CO_2 when the supply of air is restricted, so in solution, when there is insufficient oxidising agent, we obtain not an acid but a compound containing CO, which we call an aldehyde. The analogy is very close between oxidation in the air and in solution, for the acid group is $COO.H_2$, whereas the aldehyde group is CO.H. This is seen best by writing the structural formulae for the two products of oxidation of ethyl alcohol thus:

	$CH_3CO.OH$
$CH_3.CH_2OH$	Acetic acid
Ethyl alcohol	$CH_3CO.H$
	Acetaldehyde.

In these oxidations it is to be observed that the CH_3 group remains untouched, and this is good example of how one group or radicle in a compound may remain unchanged throughout a series of operations while other groups are altered. In testing for a substance in analysis it is the changeable group which we detect and by which we recognise the substance. We infer the nature of the unchanging part of the molecule rather from the physical properties of the substance.

114. Properties of aldehydes

Since aldehydes are stages on the way to acids, i.e. are only partially oxidised, we might anticipate that by further oxidation they would be transformed into acids, and such is the case. Aldehydes are therefore reducing agents. Solutions of metals such as copper and silver serve well to detect and to estimate

aldehydes for the action of the aldehyde will be to remove oxygen from the metallic oxide in solution and to form either a lower oxide which may be precipitated or the metal itself. Whether the lower oxide is formed or the metal will depend upon the extent of reduction and the readiness with which the metallic oxide used parts with its oxygen. Silver oxide, for example, readily loses oxygen, and silver is deposited; copper oxide, on the other hand, although it is fairly readily reduced to the red cuprous oxide, it is not so readily reduced to the metal, and thus only under special conditions will metallic copper be formed in reduction of cupric salts.

(*a*) To a drop of Fehlings alkaline cupric sulphate solution, add 1 drop of 40 per cent. KOH solution. Add a drop of a dilute solution of acetaldehyde (3 per cent.), and gently heat the solution. Observe the change of colour and the formation of the red cuprous oxide.

The aldehyde has been oxidised to acetic acid thus:

$$CH_3COH + 2Cu(OH)_2 = CH_3CO.OH + Cu_2O + 2H_2O.$$

(*b*) Repeat the above experiment, using a solution of formaldehyde of the same concentration. Observe that the reduction is more intense, and metallic copper, as well as cuprous oxide, may be formed.

The formation of metallic copper by the action of formaldehyde is very instructive, for it shows that formaldehyde is more powerful as a reducing agent than acetaldehyde, and this is why it is also a more powerful toxic substance, and hence a more powerful antiseptic.

The reason for the more powerful reduction in the case of formaldehyde is readily seen from the formulae, for in formaldehyde there are twice as many hydrogen atoms adjacent to CO as in acetaldehyde. If we remove one hydrogen atom from formaldehyde it is still an aldehyde. Compare the formulae:

Acetaldehyde	Formaldehyde
$CH_3.CO.H$	H.CO.H

The hydrogen atoms in the CH_3 group, we have already seen, are inert; it is only such hydrogen atoms as are attached to the CO which are active and able to bring about reduction.

Other oxidising agents may be used to demonstrate the presence of aldehydes, for example, potassium dichromate and sulphuric acid which have been used for the oxidation of alcohols.

(*c*) Repeat experiments (*a*) and (*b*), using aldehydes instead of alcohols. In this way you could readily estimate the amount of formaldehyde (formalin) present in a solution.

Note. Fehlings solution is a mixture of copper sulphate, sodium potassium tartrate and sodium hydroxide, but it is an advantage to add more alkali (40 per cent. KOH) to get a good mirror of copper by the action of formaldehyde.

Table of melting points of metal

	°C.
Mercury	−39
Potassium	+63·5
Sodium	98
Tin	232
Bismuth	271
Cadmium	321
Lead	327
Zinc	419
Antimony	630
Magnesium	650
Aluminium	658
Silver	961
Gold	1062
Copper	1083
Nickel	1452
Cobalt	1478
Iron	1530
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